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DESIGN AND CONSTRUCTION OF AN EXPERIMENTAL DIFFUSION BATTERY

By Max J. Proffitt

ABSTRACT

This paper considers some of the theory behind the design of a 20-cell experimental diffusion battery, built to study the extraction of polysaccharides from jerusalem artichokes. It presents complete structural details. The battery has a working capacity of 1 kg per cell. The cells were assembled on two floor plans; first, in a single-row straight battery with flux return line; later, in a folded row closed pattern with flux lines of uniform length throughout. In the first arrangement the battery could be divided into 2 batteries of 10 cells each; or into 2 batteries of 6 and 14 cells, respectively; or into 3 batteries of 4, 6, and 10 cells, respectively. The design of the second arrangement provides for the same options in folded units, as well as the splitting of the battery lengthwise into two 10-cell straight units, but the special fittings for multiple folded units have not been installed. Without dividing, the folded arrangement can be operated in two tandem columns which are completely independent, except as to length of charging periods. The folded arrangement provides also for a variety of special regimes of processing, including the preheating of new charges and the application of reagents at whatever point desired, for example, to control the pH during diffusion. Several diagrams of battery regimes are presented and a number of new terms are introduced to clarify the concepts and to stimulate discussion of a possibly standard nomenclature for the leaching processes in general.

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I. INTRODUCTION

This battery was built at the National Bureau of Standards in 1924 for the purpose of studying the application of the diffusion process to the extraction of the polysaccharides from jerusalem arti-

chokes as a first step in the manufacture of levulose. Although "beaker" experiments by the author in 1918 had indicated qualitatively that the process could be adapted to this purpose, to verify this conclusion a similar procedure was carried out on a quantitative basis on May 8, 1924, by R. F. Jackson and the author. The results[1] of this experiment indicated that with artichoke cossettes a term of processing may be required as much as 50 percent greater than that required for an equivalent degree of extraction of beet chips. Accordingly the experimental battery was designed with 20 cells, instead of the 14 which was then prevalent in the American beet-sugar industry. To adapt the equipment to a laboratory scale the working capacity was made 1 kg of cossettes per cell. The present paper describes the design and structure of the battery in both the original single-row arrangement of the cells, commonly known as the straight floor plan; and also in a double-row arrangement, made in 1926, which will be called the "folded-row" pattern. The general appearance of the battery in the second arrangement is indicated by figure 1. Later papers will deal with some of the experimental results obtained with the battery and its accessories.

II. STRUCTURE OF THE DIFFUSION BATTERY

A diffusion battery is essentially an assembly of multiple containers with a system of intercommunicating manifolds of pipe lines and valves arranged for the continuous extraction of soluble substances from particles of solid or semisolid materials. Usually the containers are known as cells or diffusers. The fresh particles are charged through the top opening of the cell, which is closed by a cover; and eventually the spent particles are discharged through a wide bottom opening, which is closed by the door. Most frequently the door opens

[1] The extraction was made by macerating 100 g of artichoke cossettes on a steam bath with successive changes of hot water at 5-minute intervals. In the following summary of results the relative quantities of sugar in the original cossettes, in the various extracts, and in the final residue, are indicated by the quantity of copper precipitated from soxhlet solution by the respective liquids after hydrolysis with acid.

Material	Weight of material	Weight of Cu precipitate	Equivalent extraction
	Grams	*Grams*	*Percent*
Cossettes	100.0	26.70	
Extract:			
1	103.8	8.706	32.61
2	87.1	4.575	17.13
3	106.2	3.251	12.18
4	104.3	2.239	8.39
5	98.7	1.634	6.12
6	104.5	1.155	4.33
7	103.9	1.011	3.79
8	103.9	0.776	2.91
9	104.6	0.614	2.30
10	103.0	0.589	2.21
11	100.9	0.376	1.41
Total	1,120.9	24.926	93.38
Residue	371.3	1.514	5.67
Total	1,492.2	26.440	99.05

In the commercial extraction of sugar-beet cossettes for a term of processing similar to that indicated above, only about 2 percent of the sugar introduced ordinarily remains in the residues of pulp and pulp water, whereas here nearly 6 percent remained in the pulp and water after the last digestion.

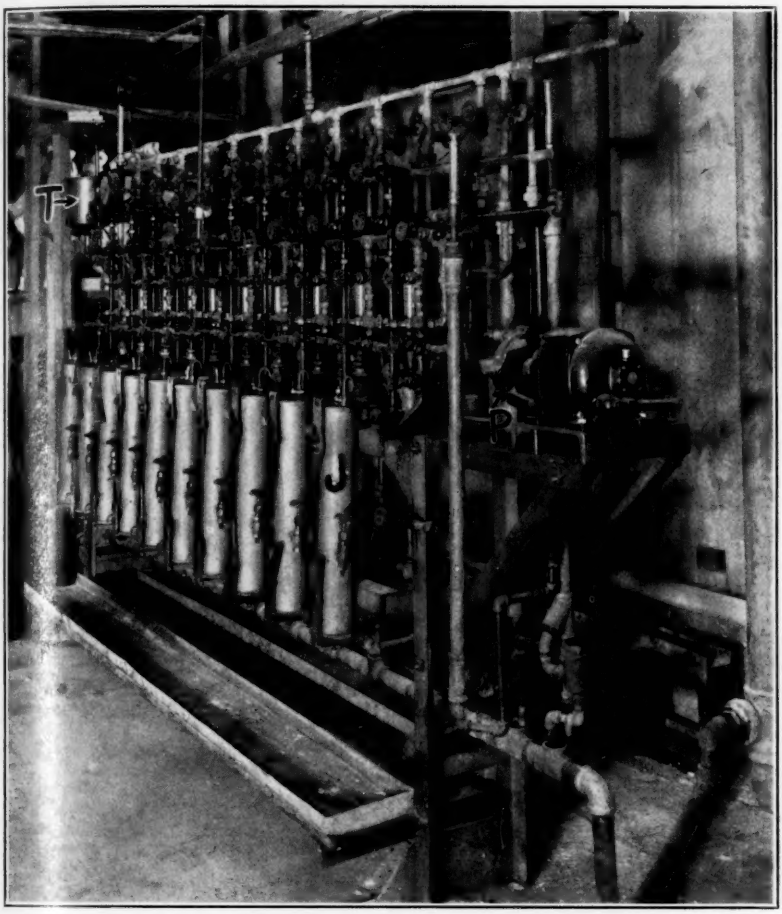

FIGURE 1.—*Battery in the folded-row arrangement.*

(See appendix for explanatory text.)

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downwards; occasionally, sidewise. In any particular installation the cells are of uniform capacity. In the beet-sugar industry the usual capacity per cell is between 3 and 7 tons of cossettes. The shape of the cell is cylindrical, usually with conical top and bottom sections, as indicated in figures 2 and 4. In the present experimental battery, however, the cells are cylindrical throughout their length and their proportions are relatively long and narrow, as illustrated in figure 1. For extracting such materials as cossettes prepared from sugar beets or from Jerusalem artichokes, each cell is provided with a means of heating the material while in process of extraction. Sometimes this is accomplished by a direct injection of steam, but more often a special surface heater, known as a "calorisator", is provided for each cell. In the diagrams of figures 2, 4, and 5 the calorisators are represented between the cells. In the experimental battery they are placed directly back of the cell, as illustrated in figures 1, 9, and 10. In the usual commercial installation they are placed about 30° from this position. In most commercial batteries, as well as in both of the experimental arrangements here discussed, each heater forms a part of the duct leading from the bottom of the cell to the flux line or manifold of that cell. The flux manifold FM in figure 5 is connected through separate valves (1) to the efflux manifold, as indicated at E in figure 5, and (2) to the inlet manifold IM of the cell next lower in the series. The flux and inlet manifolds may be considered as local or cross headers, each serving an individual cell. The solvent or water manifold, and the efflux manifold, sometimes known as the "solution header" or "juice line", are general manifolds because they serve any cell in the battery. For the same reason the circulation manifolds used in the second arrangement of the experimental battery, as indicated in sketch b of figure 5, are also general manifolds. Figure 5, sketch a, is a diagrammatic representation of the relations among the cells, the calorisators, and the various manifolds in the first arrangement of the experimental battery. It can serve as well for the usual commercial installation, except that some of these have "cell cut-out" bridge connections between the flux manifolds, which were not provided in either arrangement of the present experimental battery.

It will be observed that liquid can be admitted to any cell in three different ways: through the inlet of the cell, from either (1) the solvent manifold, by opening the valve at W; or (2) the flux manifold of the cell next higher in the series, by opening the valve at F_2; or finally, (3) through the port at the bottom of the cell, which is prevailingly the outlet for liquid, by opening the valve at E to flood the newly charged particles with extract, expel the air, and establish the requisite contact of external liquid. This initial flooding of the particles is simply one phase of the charging of the cell and in this discussion will be called the priming of the charge, or the priming of the cell. Thus a group of any integral number of successive cells less than the number of cells in the battery can be connected together by the valve openings in the transfer ducts in such a way that liquid can flow from the solvent manifold, serially through all the cells in the group, into the efflux manifold from which it passes in two directions, as stated below. In the ordinary method of battery operation, it flows nowhere else. The number of cells in the group is less than the number in the battery because at least one cell must be continually out of service to accommo-

date the operations of emptying spent charges and admitting fresh charges, including the priming liquid. From the efflux manifold the liquid is delivered partly into the draft of finished extract, and thus withdrawn from the system; and partly into the priming of new charges and therewith briefly returned to the system. The uniform quantity of extract which is withdrawn between the introductions of successive charges is known commonly as the "draft." It is varied to suit the concentration of extractives in the fresh particles and the conditions of operation; but it is practically the same whether the drawing is accomplished concurrently or alternately with the priming.

The valve settings required for any particular case can be inferred from the diagrams of figure 5 and the assembly drawings of figures 9 and 10. Notice that the valve stems of the experimental battery look out from a panel-like arrangement above the cells, while those of a commercial battery generally look up from the floor near the level of the top openings of the cells.

The program of conditions which operate upon each successive charge of material during the term of its processing will be called the regime of operation for that run. The regime of operation includes the course of the solvent as directed by the settings of the valves, the temperature schedule, the proportionate quantity of draft, and all the other applied conditions, as well as the consequential conditions which result from the application of the method to the materials.

III. ACTION OF THE DIFFUSION BATTERY

In effect, a diffusion battery is a countercurrent percolator or leacher. The new charges are introduced at regular intervals, here called charging periods, and simultaneously the spent charges are abandoned at the opposite end of the series of active cells. Thus each charge enters the extraction system in the first posture or grade of the series, and remains in this posture during the whole first period of its treatment. During the second period it occupies the second posture; during the nth period the final posture. The water or other solvent is introduced to the most nearly spent charge, passed from cell to cell, and finally, as finished extract, withdrawn from the cell containing the newest charge. Thus during the whole term of processing, except the last period, each charge receives a continuous influx of liquid discharged from the contiguous older charge. During the last period it receives a continuous influx of fresh solvent.

Solvent in contact with particles of any degree of exhaustion, or that anywhere in transit between charges, thus containing a smaller or greater concentration of extractives, will be called flood liquid. The flow which carries it from cell to cell, and thus works the changes wrought by the process as a whole, will be called the flux. Although local flows of much larger volume may assist in the work or may even bring about indispensable effects, the flux is the fundamental operator. The method of its action will depend upon whether the flux is continuous or intermittent and whether it is integral or partial; the possible variations are too numerous to discuss exhaustively. The flux is integral when the flood liquid in all of the cells is propelled toward the extract outlet as one intact mass in such a way that its motion comprehends all of the relative movement between particles and flood liquid. It is partial when it does not comprehend all of

this motion, but is superimposed upon or alternated with a local circulation of the flood liquid or a local agitation of particles and flood liquid produced independently of the flux. The two types are compared diagrammatically in figure 2.

The relation of the battery to the process may be presented in two aspects, and the importance of each relative to the other depends largely upon the method of operating the flux. In the "standard" method of operation, as applied to the diffusion process in the beet-sugar industry, the flux is integral and practically continuous. The whole series of active cells may be regarded as a unit column of n cells' length because the residual extractives in the sap, and likewise

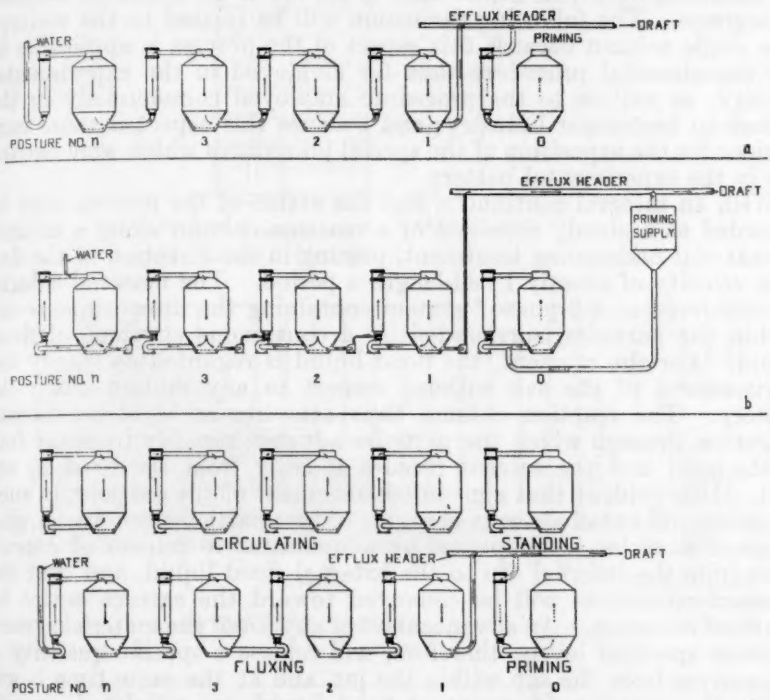


FIGURE 2.—*Flow diagrams for three different regimes of diffusion-battery operation.*
(See appendix for explanatory text.)

the accumulated extractives in the flood liquid, become distributed along a smooth concentration gradient extending from the solvent inlet at the head of the column [2] to a region somewhere near the extract outlet at the foot, as indicated diagrammatically at a in figure 3. There are no considerable discontinuities at cell boundaries. With a partial flux, on the contrary, there must be such discontinuities, and in the extreme case of very extensive local circulation or perfect local mixing, there will be no lengthwise gradients through each cell. The concentrations from one end of the series to the other will vary stepwise, as indicated at b in figure 3. Then the active cells may be seen more conveniently as a battery of separate batch

[2] The water inlet is sometimes known as the "tail of the battery", sometimes as the "head". All ought to be agreed as to which is the head and which the foot of a percolator column.

percolators containing systematically exhausted charges which operate upon the passing flood liquid, and upon which the flood liquid operates.

When the partial flux is continuous the attenuation of the concentration of extractives in each phase of each cell's contents will be continuous with the lapse of time, as illustrated at c in figure 3. It will be similar to the attenuation obtained with a continuous integral flux, notwithstanding the stepwise distribution of the concentrations along the battery. The aspect of the process which is connotated by the idea of a battery of separate batch extractors will not be considered further in the present discussion, although that aspect applies with equal strength whether the distribution of concentrations must be described by a pair of continuous curves or by a pair of stepped histograms. The following discussion will be related to the concept of a single column because this aspect of the process is applicable to the experimental procedure thus far employed in the experimental battery, as well as to the procedure employed commercially in the American beet-sugar industry; and because this aspect is more convenient for the exposition of the special procedures which were carried out in the experimental battery.

With an integral continuous flux the action of the process may be regarded as a steady recession of a reaction column along a column of material undergoing treatment, passing in the direction of the flux at a velocity of exactly 1 cell-length a period. The material column is considered as a 2-phase [3] system containing the discontinuous sap within the particles, surrounded by a continuous envelope of flood liquid. For the moment, the flood liquid is regarded as simply the environment of the sap without respect to any motion along the battery. The reaction column thus acts like an ideal continuous extractor through which the particles advance steadily from the foot to the head and the solvent recedes steadily from the head to the foot. It is evident that a given advancement of the particles in such a column will entail a steady charging of new particles and discharging of spent particles, accompanied by a quantitative release of extractives from the internal sap to the external flood liquid, and that the released extractives will be conveyed toward the extract outlet by the flood recession. An advancement of any jot of the material system between specified levels, therefore, will release a specific quantity of extractives from the sap within the jot, and at the same time it will dilute the sap's environment of flood liquid by a related specific amount. Thus in a battery column the flux velocity is the sum of the velocity of virtual advancement of the chips toward the head of the reaction column, plus the velocity of virtual recession of the flood liquid toward the foot. The recession is measured by the net rate of discharge of the flood liquid from the system; and it is conveniently expressed as a lengthwise displacement of the flood column, although more commonly expressed as a percentage of the weight of the cossettes charged. The very fact that the reaction column virtually must be fed with the particles continuously, while the material column is charged by cellsful, indicates that there must be always some disparity between the character of the process as a whole and the state of the material in the lower end of the battery column. This disparity can be augmented by inadequate heating at the foot of

[3] For the present purpose the marc need not be regarded as a third phase. Operatively it is a part the apparatus which supports the sap and may sometimes act as a dialysis membrane as well.

the column, as will be seen later; and the result is such as that indicated by the two pairs of attenuation curves presented at a and c in figure 3.

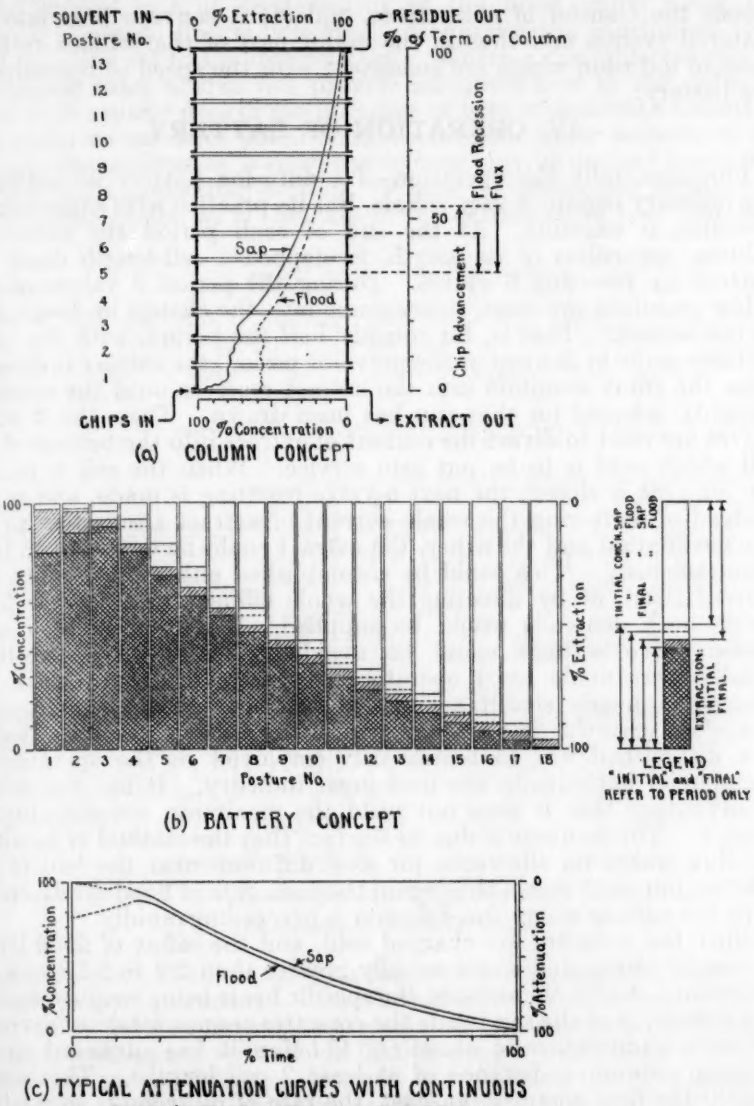


FIGURE 3.—*Concepts of diffusion-battery performance.*
(See appendix for explanatory text.)

An integral continuous flux in a diffusion battery column of the ordinary type operates in four distinct ways: (1) It propagates the diffusion of extractives. This is done by maintaining a continuous dilution of the flood liquid associated with any jot of the chips where

a correctly poised relationship among the working conditions has become established. (2) It conveys the diffused extractives out of the system; (3) it limits the thickness of the diffusion layers through its erosive action on the surface films of stagnant flood liquid, and thus speeds the transfer of extractives, and (4) it conveys heat into the material system and thus in the major part of the column sustains rates of diffusion which are consistent with the speed of operation of the battery.

IV. OPERATION OF BATTERY

Fundamentally the operation of a diffusion battery according to the ordinary regime is very simple, but its practice with experimental precision is exacting. At the end of each period the extraction column, regardless of its length, is stepped 1 cell-length down the battery by resetting 6 valves. During the period 2 valves on the efflux manifold are reset to accommodate the change in destinat of the extract. That is, for roughly half the period, with the valve settings made at the end of the previous period, the extract is directed from the efflux manifold into the extract receiver until the constant quantity selected for that run has been drawn. Then the 2 efflux valves are reset to divert the current of extract into the bottom of the cell which next is to be put into service. When the cell is primed the air vent is closed, the next 6-valve resetting is made, and so on. Instead of delivering the whole current of extract alternately to the one destination and the other, the extract could be delivered to both simultaneously. This could be accomplished either by dividing the current itself, or by directing the whole effluent to a storage from which both demands would be supplied. By either method mid-period valve settings could be avoided. The 6-valve resettings usually were made by 3 operators who were drilled to make the changes as nearly simultaneously as possible. In the experimental procedure with the first arrangement of the battery, the only type of flow established was that ordinarily employed in the operation of commercial batteries in the beet-sugar industry. It has the serious disadvantage that it does not yield the maximum concentration of extract. The wantage is due to the fact that the method of handling the flux makes no allowance for slow diffusion near the foot of the column, but produces in this region the same rate of flood displacement as in the regions where the diffusion is proceeding rapidly.

Since the cossettes are charged cold, and the influx of flood liquid by weight per period is not usually greater than 2.2 to 2.5 times the weight of a charge of cossettes, the specific heats being roughly similar, it is evident that the sap inside the cossettes cannot attain a favorable diffusion temperature of about 80° C before it has advanced up the reaction column a distance of at least 2 cell lengths. This means that in the first postures, at least, the rate of diffusion is so small as to justify but a small fraction of the rate of displacement of the flood liquid along the column permissible in the "diffusion zone", comprising the upper major part of the column where favorable temperatures and correct concentration gradients have become established. On the other hand, for carrying the requisite quantity of heat into the new charges the most favorable rate of flow of the flood liquid is the maximum which can be applied without seriously disturbing the "packing" or mass-structure of the properly deposited chips. This

rate is at least equal to the permissible rate of flux through the diffusion zone.

In general, where the optimum velocity of relative motion between the flood liquid and the particles is much greater than the most advantageous rate of displacement of the flood liquid along the column, a partial flux is indicated. Generally the continuous type is to be preferred to the intermittent. Where a desirable velocity of continuous integral flux will provide adequate flow in the diffusion zone, as it usually does in the diffusion of beet or artichoke cossettes, but produces excessive phase translation in the lower sections of the column where diffusion is slow, the column may be divided into a flux section and a preheating section. Where the preheating section can be relatively short, as is the case in the extraction of beet and arti-

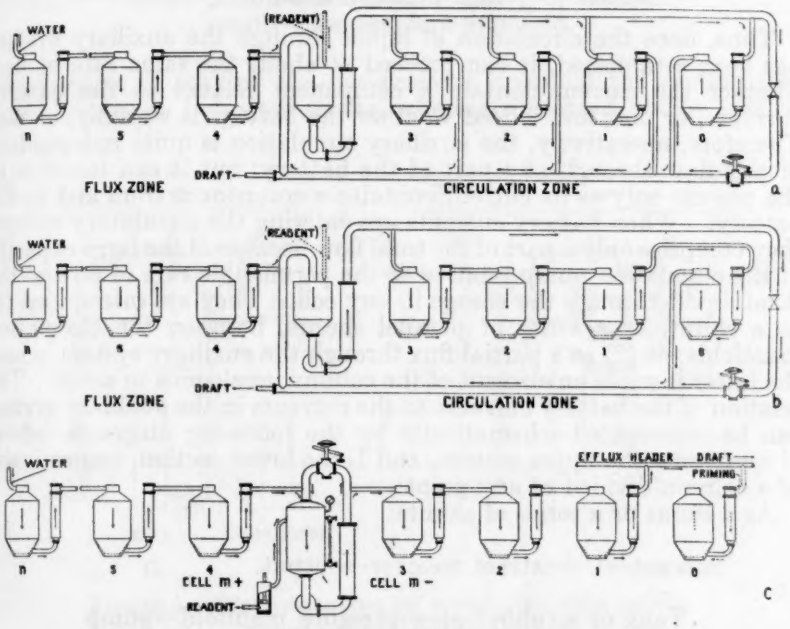


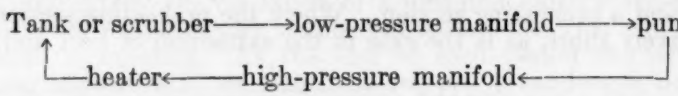
FIGURE 4.—*Flow diagrams with the circulatory system.*

(See appendix for explanatory text.)

choke cossettes, the flux through this section can be reduced to zero for all practical purposes. Then the effluent will be withdrawn from the foot of the flux section of the column and directed either into a general extract receiver and circulation supply tank from which the draft of extract or diffusion juice will be withdrawn; or what is nearly equivalent, into the low-pressure circulation manifold from which the draft may be withdrawn as desired; or alternately into the circulation supply and draft receiver. In the preheating section the hot extract will be circulated through the cells, preferably in parallel, as indicated diagrammatically at a in figure 4, although the operations of valve setting can be simplified somewhat by circulating the liquid serially through the cells, as suggested at b in figure 4.

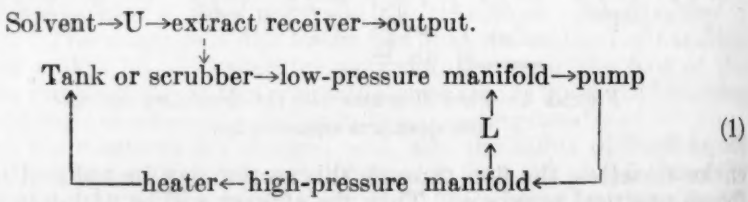
V. AUXILIARY CIRCULATORY SYSTEM

In the folded arrangement of the battery an auxiliary circulatory system is provided for the establishing of this effect, as well as for a variety of other purposes. The principal parts of this auxiliary are the high- and low-pressure circulation manifolds; the circulation pump; the pump supply tank, in place of which a scrubber or gas-absorption tower can be substituted; and a special heater installed in the high-pressure circulation manifold near the tank or scrubber. The flow of liquid through the auxiliary system as it was actually installed (fig. 5, b) is illustrated by the scheme:



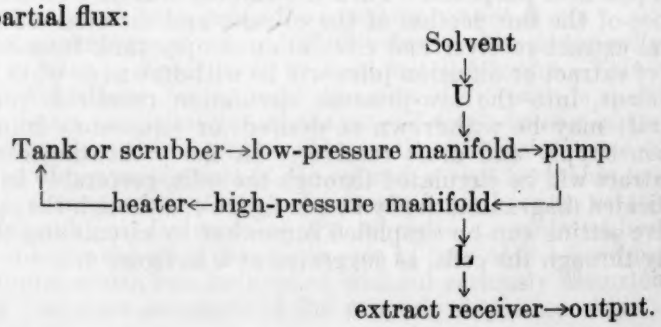
Thus, once the circulation of liquid through the auxiliary system has been established, it can proceed at about the same rate of flow whether the current contain a component related to the battery currents, or not; and indeed whether the battery is working, or not. Therefore, operatively, the auxiliary circulation is quite independent of any flow through any part of the battery; but it can function in the process only as its current contains a component from and to the battery. When battery currents are entering the circulatory current they comprise only a part of the total flow because of the large capacity of the circulation pump relative to the permissible rate of flow of the flood liquid through the charge in any cell. They are introduced (1) as a shunt, or a series of parallel shunts, between the circulation manifolds; or (2) as a partial flux through the auxiliary system, where the latter is made an element of the column, analogous to a cell. The relation of the battery currents to the currents in the auxiliary system can be represented schematically by the following diagrams, where U represents the upper section, and L the lower section, respectively, of a column divided at any point:

As a shunt or a series of shunts:



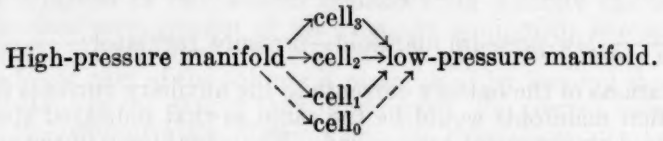
(1)

As a partial flux:



(2)

When preheating is applied to any group of cells in parallel (fig. 4, a), the circulatory flow through the group comprises so many shunts between the circulation manifolds, thus:



When preheating is applied serially (fig. 4, b), the flow is a single shunt between the manifolds, thus:

High-pressure manifold→$cell_3$→$cell_2$→$cell_1$
→$cell_0$→low-pressure manifold.

The purpose of making the low-pressure manifold the suction line of the pump, as indicated in the schemes presented above, was to

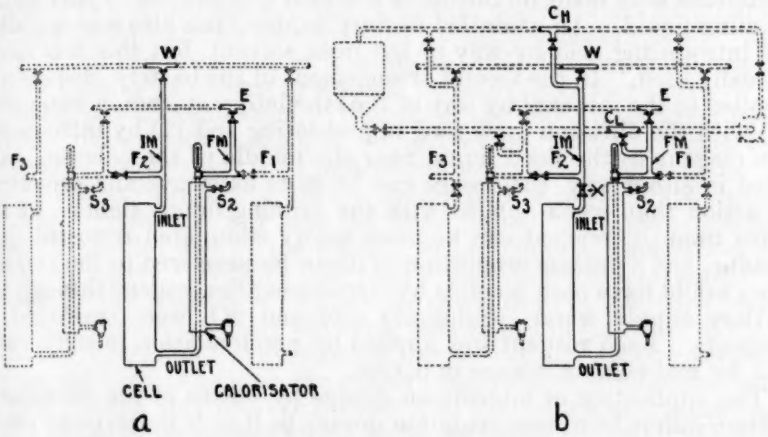


FIGURE 5.—*Pipe connections, (a) straight, (b) folded battery.*
(See appendix for explanatory text.)

maintain the pressure head between the manifolds at the practically constant value generated by the pump. Experience indicates that it would have been wiser to place the pump in the position originally selected, directly under the tank, to which it would have been connected by a short suction line, and to connect the 2 manifolds at the opposite end through (1) a stop valve, for complete separation when required, in series with (2) a throttle valve or an adjustable automatic pressure regulator, for control of the pressure differential between the manifolds according to the varying needs of different regimes of operation, all as indicated diagrammatically in figure 4. Then the priming could be accomplished almost automatically by introducing the circulatory flow into the bottom of the cell in posture 0, thereby gaining over the ordinary method of priming a better elimination of air and

perhaps half a period longer time of heating. The flow through the circulatory system then would be described by the scheme:

Tank or scrubber——→pump——→heater——→high-pressure manifold
↑ ↓
└———low-pressure manifold←pressure regulator←———┘

The relations of the battery currents to the auxiliary currents in the 2 circulation manifolds would be the same as that indicated above for the revised arrangement as installed. The advantages of the arrangement as originally devised, over the revised arrangement of the auxiliary system, have been demonstrated on a larger experimental battery. Figure 4 illustrates the original plan, figure 5 the way the system was installed.

VI. REAGENT DOSAGE

The circulatory system has been used in applying a special treatment which may be called a "dosage" of the material with a reagent. With the straight arrangement of the battery some inconclusive experiments were made on the use of acidified ("converter") juice as the priming liquid. An enameled battery supply tank also was installed for introducing acid by way of the fresh solvent, but this was never actually used. In the second arrangement of the battery, dosage was applied to the material by way of the circulatory system in two ways: (1) with the diffusion juice used in preheating and (2) by introducing the reagent to the flood liquid near the middle of the column. Applied in either way, the dosage can be more extensive and prolonged in action than when applied with the priming liquid alone. At the same time the reagent can be more nearly eliminated from the final residue, and a greater proportion of it can be recovered in the extract, than would have been possible by introducing the reagent through the battery supply water. Sulphuric acid and SO_2 were employed as reagents. Each reagent was applied by precirculation in some cases and by mid-column dosage in others.

The application of midcolumn dosage by means of the circulatory system differs from precirculation dosage in that it involves no circulatory flow through a section of the column. Instead, the flux between two postures near the middle of the column is conducted as a partial flow through the circulatory system where the flood liquid involved becomes impregnated with the desired reagent to the preselected concentration. A diagram of the flow is presented at c in figure 4. The dosage could be produced as well by injecting the reagent at correctly measured rate into the appropriate flux line, or even into a cell; which is to say, it could be injected into the current of flood liquid at any desired "level" along the column. The level at which the dosage is to be applied, by whatever means, will be selected according to the character of the reagent and according to the relative weights assigned to the duration of the action of the reagent as opposed to the degree of its elimination. Ordinarily a level somewhere near the middle of the column will be selected; hence the name. The relation of the circulatory system to the column in this regime is indicated by the scheme:

Effluent from $cell_{m+}$——→ low-pressure manifold——→ high-pressure manifold (as partial flow)——→ $cell_{m-}$,

where $cell_{m+}$ is the diffuser situated in the first posture above the point of application of the treatment, $cell_{m-}$ that in the first posture below the point of application. The locations of the pump and the tank or scrubber in this scheme depend upon whether the original or the revised arrangement of the auxiliary equipment is employed.

In either case the correct rate of flux out of the circulatory system into the lower part of the column is maintained by keeping the liquid level constant in the supply tank or scrubber; the correct dosage, by keeping the concentration of reagent in the circulating liquid practically constant. The concentration of extractives in the liquid becomes nearly constant also because the flux of the flood liquid through the auxiliary system is a minor component of the total current in the unit, as previously explained. The flood liquid enters the lower section of the column with no considerable gradient of extractive concentration, such as it had before entering the auxiliary, but an effective gradient is soon recovered in recession. Reagent dosage by injection would involve no disturbance of the gradient and no risk of a considerable variation of the rate of flux such as can result from variations in the quantity of liquid impounded in the circulatory system. It will be observed that a certain degree of acidification of the flood liquid could be accomplished by electrolysis in transit. For this purpose the operation of a series of small flux line units would seem at least as promising as a single outside circulatory unit.

The highest concentration of reagent in the flood liquid must exist near the place of application in either method. This produces the remarkable result that, with midcolumn dosage, the net transfer of reagent is first "inward" from the flood liquid to the sap, and finally "outward" from the sap into the flood liquid. The inward trend extends from the foot of the column to the point of application, or somewhat above. Within this region the diffusion of reagent is opposite to the transfer of the natural extractives of the chips, since the latter is predominantly outward, just as in the standard method of battery operation. Nevertheless, because of the greater activity of a reagent such as an acid, the relative degree of its elimination from the final residue may be even greater than that of the natural extractives. Midcolumn dosage seems to be indicated where a prolonged action is to be combined with maximum recovery of reagent, or with minimum contamination of the residue. It should prove especially serviceable in the control of pH during the diffusion of any material where such control seems advantageous; to the application of a reagent for retarding fermentation in low-temperature diffusion; for fixing proteins during diffusion; and for many other purposes. No similar regime seems to have been applied in the beet-sugar industry, and apparently it is new.

VII. MULTIPLE COLUMNS

In either the straight or the folded arrangement the experimental battery could be operated as a single extraction column of any number of cells from 2 to 19, inclusive. The possibility of having as few as one cell unengaged is due to the fact that during even the minimum practical operating period of about 4 minutes, a spent charge could be emptied, the cell cleaned, refilled with cossettes, and primed for reentry into the column. To provide for direct comparison of the relative

effects of different regimes with respect to any particular factor, either arrangement of the 20 cells could be divided among 2 or 3 independent shorter batteries; or, without dividing into completely independent units, 2 columns could be run in tandem around the whole 20-cell circuit. Theoretically tandem columns could be run in any standard diffusion battery, but the division into smaller units requires special fittings: (1) For bridging between certain cells and the flux return line, in the straight battery; and between contiguous cells in different rows, or between the opposite ends of each row, in the folded arrangement; and (2) for dividing the flux return line and efflux and circulation manifolds into sections. If multiple columns are operated commercially at present, by either method, the practice certainly is not common. Tandem columns could be applied for increasing the capacity of a battery, with some sacrifice in extraction. They could be applied also in some of the complex extractions which have been described.[4]

In either arrangement of the experimental battery, tandem columns of equal length or of different lengths could be operated; but of course only on the same period-schedule for both columns. Obviously, when 2 columns are operating, at least 2 cells must be out of engagement for the emptying and charging operations. Thus the maximum number of cells engaged in the 2 columns is 18. In the first arrangement the two effluents could not be kept wholly separate. In the second arrangement, thanks to the extra manifolds available, the two effluents can be taken off separately. For example, the performance of a column with a preheating section can be compared directly with the performance of a standard column with the same or a different total term of processing, depending upon the distribution of the cells between the 2 columns.

The manner of dividing the battery into two or three independent units seems sufficiently evident for either arrangement of the experimental battery. Some of the special valves and connections required for dividing the straight battery are indicated in figure 9; and for dividing the folded battery, in figure 10. In either arrangement the design permits the following optional groupings of the cells: Two 10-cell batteries; two batteries of 6 and 14 cells, respectively; or 3 batteries of 4, 6, and 10 cells, respectively. In the first arrangement the shorter units were necessarily of the straight type; in the folded arrangement shorter units of either the straight or the folded type are possible. In the second arrangement the battery can be split lengthwise into 2 straight batteries of 10 cells each, for which a pair of flux return lines is provided to bridge between the opposite ends of each row. These are indicated in figure 10, partially revealed in figure 1. Because tandem columns could accommodate nearly every duplex experiment that it seemed wise to undertake, the special bridge connections between the rows and the special manifold fittings, for dividing the folded battery into smaller folded units, have not been installed. The fundamental simplicity of the pipe connections, per cell, for the two arrangements of the battery is indicated in figure 5. The connections required for dividing the battery into the various optional groupings specified, constitute but slight complications, and these at certain points only.

[4] For example, such an extraction as that described by Schreiber, Geib, Wingfield, and Acree, Ind. Eng. Chem. 22, 497–501 (1930).

The alterations recommended for new installations of the folded arrangement of a diffusion battery for experimental purposes are: (1) The placing of the circulation pump directly under the tank and the provision of the pressure regulator already mentioned; (2) the insertion of stop-valves at position X, figure 5, if it is desired to operate 3 columns in tandem; (3) the installation of thermometers at the centers of the cells in place of, or in addition to, those indicated at the tops of the heaters; (4) the replacement of the manually operated valves required in routine operation, with valves operated by air or water pressure, or by electric circuits, actuated by an adjustable device upon which automatic or semiautomatic programs could be set up as desired. The latter is to be considered only where the probable increase in precision, and the relief from the tedium of manual operation, outweigh the very considerable expense involved.

VIII. FLOOR-PLAN PATTERNS

For maximum precision in the flux of the flood liquid, the best floor-plan arrangement of the cells may be classed as the closed patterns where the flux lines are all of uniform length. Of these the most obvious is the familiar circular plan; the most economical of space and the most convenient to construct with standard pipe fittings, as well as the one practical arrangement which is capable of division into shorter closed units, is the folded-row plan. A battery of this type is essentially a collapsed circular battery. The single-row arrangement requires one long flux return line to bridge between the ends, and this results in certain irregularities or unsteadiness of performance which may be inconsequential in industrial practice, but should be avoided in experimental procedure. This drawback, and the additional one of conducting the flux integrally through the incompletely heated lower section of the column, became apparent in the very first experiments with the battery. These considerations, coupled with the desire to experiment more effectively with reagent dosage, led to the design of the folded arrangement of the battery with the circulatory system as described.

IX. CONSTRUCTION OF THE EXPERIMENTAL BATTERY

To accommodate acid dosage, within the buffering capacity of the artichoke sap, all metallic parts of the battery which could come in contact with the cossettes or flood liquid were constructed of brass, copper, or monel metal. The cells were made long and narrow to provide a maximum linear velocity of the flux at any particular rate of translation of the flood column. The inoperative retention of the flood liquid, which is that proportion of the total time of passage during which the liquid is not in contact with the particles, was limited to the order of that obtained in industrial installations by making the flux transfer lines of ⅜-inch pipe and incorporating as great a proportion of each flux line as possible into the single-pass calorisator attached to the cell. Undesired heating through back pressure of steam from other heaters is avoided by discharging each heater trap into a common condensate manifold which is open to the atmosphere. More accurate control of temperatures near the head of the column could have been attained by discharging the

traps through a closed water-cooled manifold into a vacuum drip receiver. Details of the construction and assembly of the parts of the battery are presented so fully in figures 6 to 10, inclusive, that no further description seems necessary.

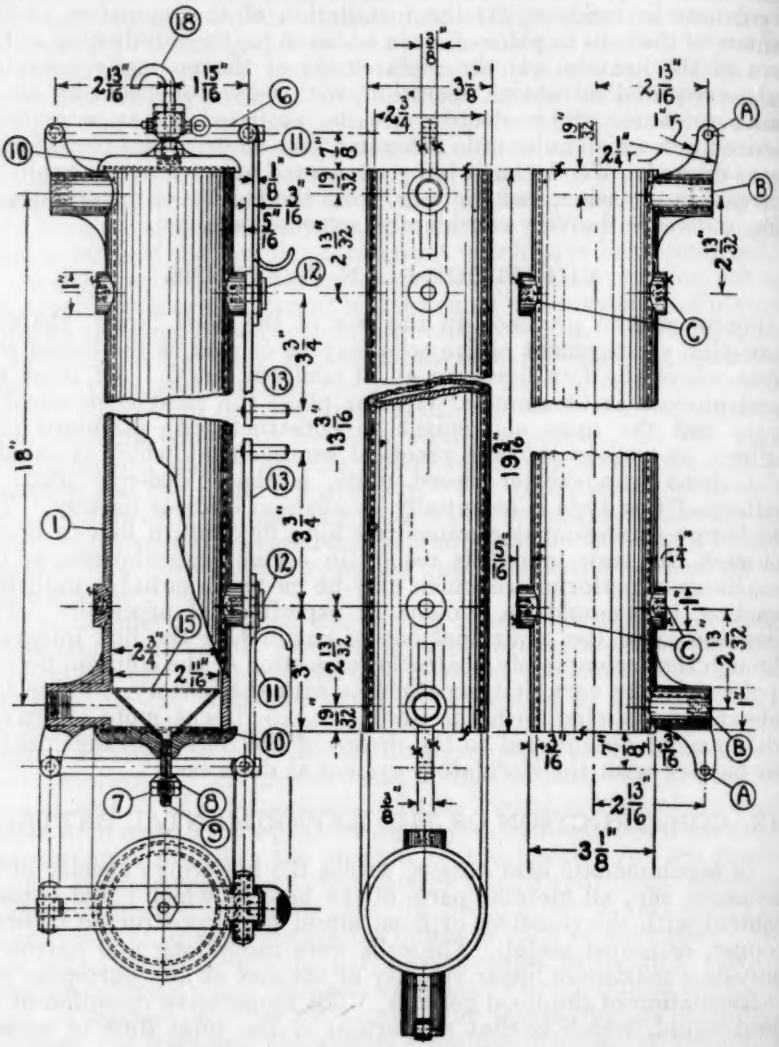


FIGURE 6.—*Cell body, cast brass.*
(See appendix for explanatory text.)

X. ACCESSORIES

The charging funnels, of which three were provided, are for convenience in introducing equal charges of cossettes without undue risk of accidental loss of material. Their construction is indicated in figure 8. The charge is weighed in the funnel with the gate

closed; after setting the funnel into the top of the cell and opening the gate, the charge is pushed into the cell and evenly packed with a wooden rod. In many of the experiments the charges were not

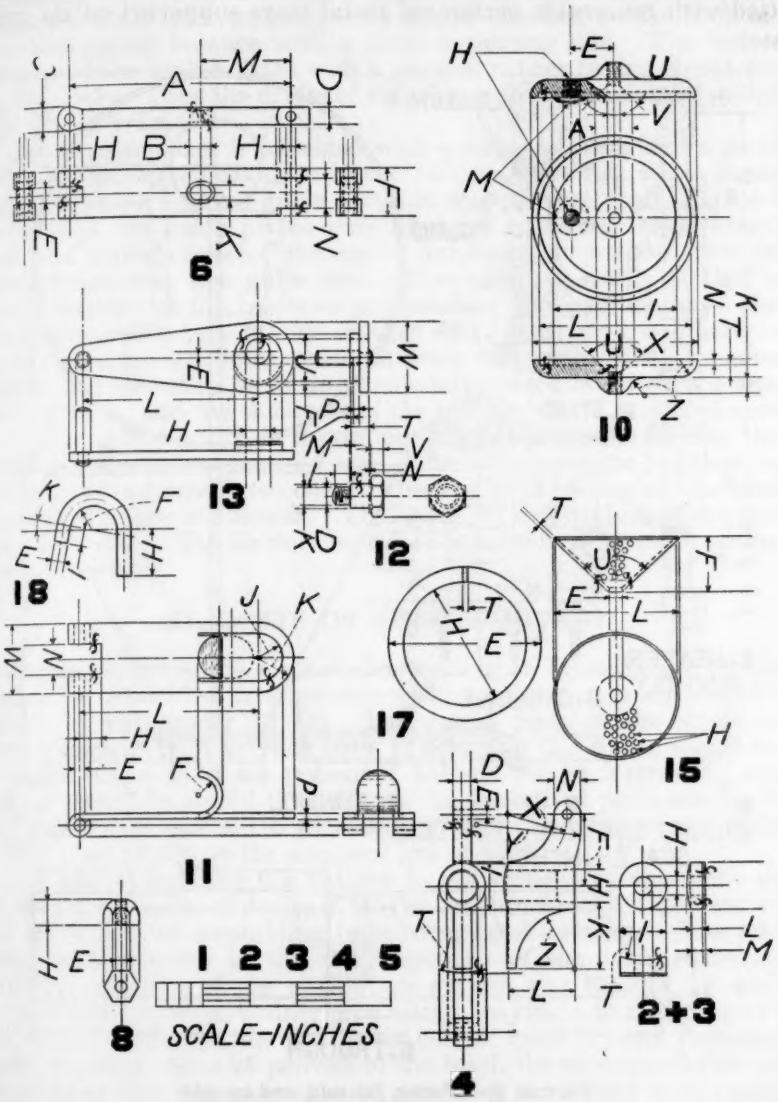


FIGURE 7.—*Cell attachments and fittings.*
(See appendix for explanatory text.)

weighed individually; in others, although the charges were weighed individually by difference, no effort was made to keep the weights uniform from cell to cell. Instead, the stress was placed on uniform packing to the very top of the cell. Even for this purpose the funnels

proved useful. All of the funnels were adjusted to the same tare weight and a special brass counterpoise was provided.

The sample receivers consist of 12-quart buckets of galvanized or enameled iron, the latter for use with acidified material. They are fitted with removable perforated metal trays supported on the rims

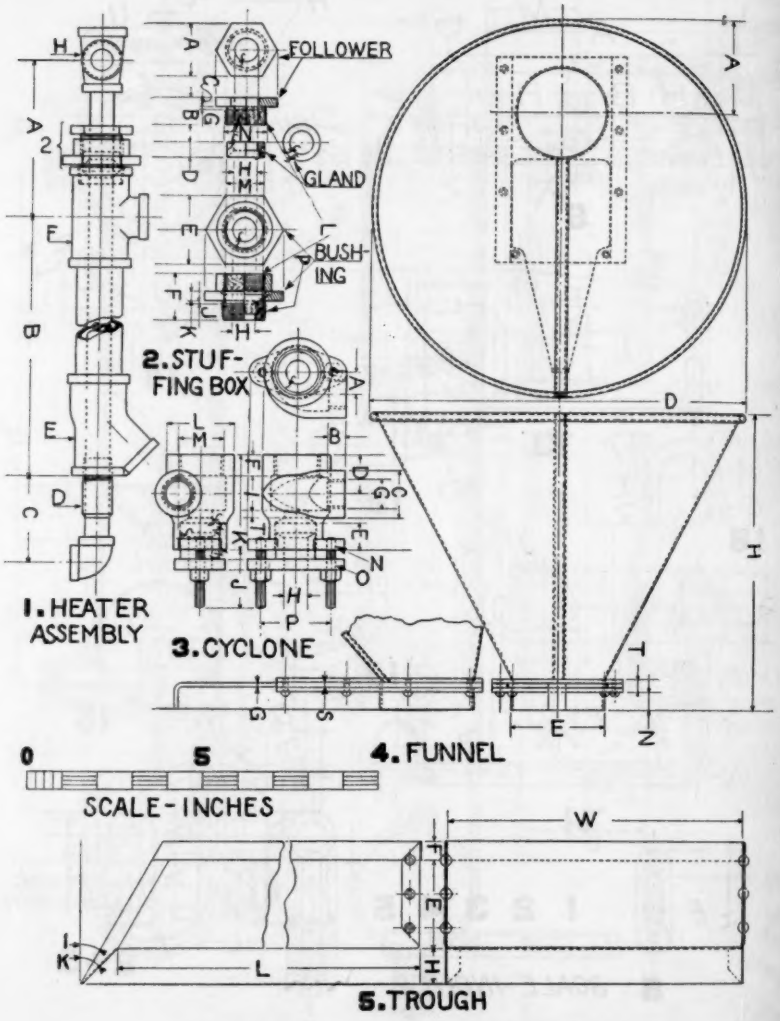


FIGURE 8.—*Heater, funnels, and troughs.*
(See appendix for explanatory text.)

of the buckets by means of attached hook-shaped supports; or instead, with conical woven wire baskets of a size and slope which will permit them to rest in the top of the bucket with the tip some 3 inches above the bottom of the bucket. The purpose of either type of tray is to retain the chips of the sample and allow the associated flood liquid to drain freely and promptly into the bucket. Each sample receiver

was tared with and without the tray, and each sample was weighed complete and with the tray of drained chips removed.

The draft receiver, or extract receiver, which corresponds to the measuring tank of the beet-sugar industry, consists of a small conical-bottomed brass tank, suspended by means of a bail on the hook of a sensitive spring balance with a large indicating dial. The bottom opening of the tank is fitted with a piece ot rubber tubing closed with a pinchcock. Thus the drafts of diffusion juice were taken by weight and not by volume.

The cossette slicer is provided with a single beet-knife of a standard type, having 30 divisions in the 13.7 cm of width, which is supported between grooved guide plates in a special reciprocating block. Grooves in the guide plates were intended to be registered exactly with the corrugations of the knife; but owing to a shop error this specification was not quite met. The principal result is that an undue number of the cossettes produced by the machine have skew dimensions, although otherwise they are of as good a quality as could be expected from material such as artichokes. In cross-section the cossettes were approximately 0.46 cm across the open part of the V, and the thickness of the limbs of the V averaged about 0.14 cm. Although their maximum length was about 10 cm, their mean length was less than 1.2 cm. When the machine is operating, the tubers are forced into contact with the knife by means of a hand-operated plunger or follower. The elevation and backset of the knife are adjustable. The knife is bolted to a hinged plate and no rocker bar is employed.

XI. COSTS OF CONSTRUCTION

At present prices the costs of constructing an experimental battery similar to the folded arrangement with circulatory system complete should be well under $2,000. The actual costs of the single-row arrangement in 1924 and the costs of changing this to the folded-row arrangement in 1926 are presented below. As an interesting sidelight it should be stated that bids on the advertised proposals for the construction of the cell bodies and calorisators alone varied rather evenly from $2,500 to the accepted low of $545.

The cost of building the battery in the straight arrangement was $1,406.08, exclusive of design. Of this amount nearly 20 percent was the labor cost of assembling, pipefitting, and painting. The additional cost incurred in the rearrangement of the same equipment with the addition of the circulatory system was $339.13, of which $175.00 was for labor, mainly pipe fitting, making a final total cost of $1,745.21. Although the final labor cost of assembly and rearrangement was thus about 25 percent of the total, the necessary labor cost would have been not more than 20 percent if the second arrangement had been resorted to at first. To the cost of $1,745.21 should be added the cost of the particular unit employed for containing the circulating liquid in the special regimes; about $26.00 for the scrubber and about $3.00 for the small open tank. This completes the cost of the battery proper.

To the cost of the battery there should be added the cost of the accessories, of which the largest item, $399.45 for the slicer, is prob-

ably excessive. The cost of the 3 charging funnels was about $30.00, exclusive of design. The sample trays cost from $0.50 each for the lightest woven wire basket to $3.92 each for the 6 perforated metal trays with hook supports. The buckets cost from $0.50 to $2.00 each. From 6 to 20 sample receivers were used. The draft receiver tank was made in the laboratory at a cost of about $1.00. The spring balances carried no charge, but probably, if new, would have cost about $10.00.

XII. CONCLUSION

1. A practical method has been devised for the heating of the fresh charges in a diffusion battery independently of the conduct of the diffusion process proper, and this results in extracts of higher concentration. The heating can be accomplished without excessive rates of flow, which would disturb the packing of the material in the cells.

2. A new method has been devised for applying a reagent to the material, allowing an extensive duration of contact together with extensive elimination of uncombined reagent from the residue and the recovery of it in the extract.

3. The application of multiple extraction columns in a single battery has been outlined (*a*) for the comparison of different regimes of operation, either by division of the battery into completely independent units or by operating the columns in tandem around the same circuit; and (*b*) for the conduct of complicated systems of extraction with different solvents, by operating the columns in tandem over a single circuit. These, and other procedures for which the battery provides, bring out the possibilities of distinct improvements in the design of extraction equipment, especially in its application to new uses.

XIII. APPENDIX

1. DESCRIPTIVE LEGENDS TO ACCOMPANY FIGURES

FIGURE 1.—*Battery in the folded-row arrangement.*

The open circulation tank T is in place at the far end; the circulation pump P at the near end. Reading from the top downward, the horizontal rows of ¾-inch valves in the panel-like mass arrangement above the long cylindrical cells J are of the kinds and for the purposes indicated below:

Row 1, globe valves connecting the steam manifold with the calorisators and heaters; row 2, angle valves connecting the solvent manifold with the inlet manifolds; row 3, cross valves connecting the high-pressure circulation manifold with the inlet manifolds; row 4, gate valves connecting the efflux manifold with the 20 flux manifolds; row 5, cross valves set at a conspicuous angle with the plane of the panel and connecting the low-pressure circulation manifold with the flux manifolds; row 6, gate valves connecting each of the 20 flux manifolds with the inlet manifolds of the next succeeding cell.

The valves applied to the sides of the cells, below their middles, are for the sampling of the flood liquid. They are not indicated in any of the drawings. Other parts can be identified by comparison of this figure with figures 5, 6, 7, and 10.

FIGURE 2.—*Flow diagrams for three different regimes of diffusion-battery operation*

Only the lines actually in service are indicated. The flow with an integral continuous flux is illustrated at a; with a continuous partial flux at b; and with an intermittent partial flux, where the flux is operated integrally while it is flowing, but alternately with local circulations, is illustrated at c.

FIGURE 3.—*Concepts of diffusion-battery performance.*

At a all of the operating cells (diagramed as very short and wide) are supposed to constitute a single extractor column, as though all of them were placed end to end. A graph of the attenuation of the sap and flood with lapse of processing time coincides with a graph of the distribution of concentrations along the column, the latter moving downward 1 cell-length during a period.

At b the operating cells are conceived as constituting so many individual percolators or extraction columns containing charges in various but systematically related degrees of exhaustion. The gradient of extractives-concentration in each liquid phase, from end to end of a cell, may be anything from zero to a gradient which is perfectly continuous with the gradients through the contiguous cells. This concept is especially useful where the flux is partial, but of course applies to any case. Whether the flux be integral or partial, so long as it is continuous the attenuation of the concentration of extractives in each phase in each cell is continuous, as indicated at c.

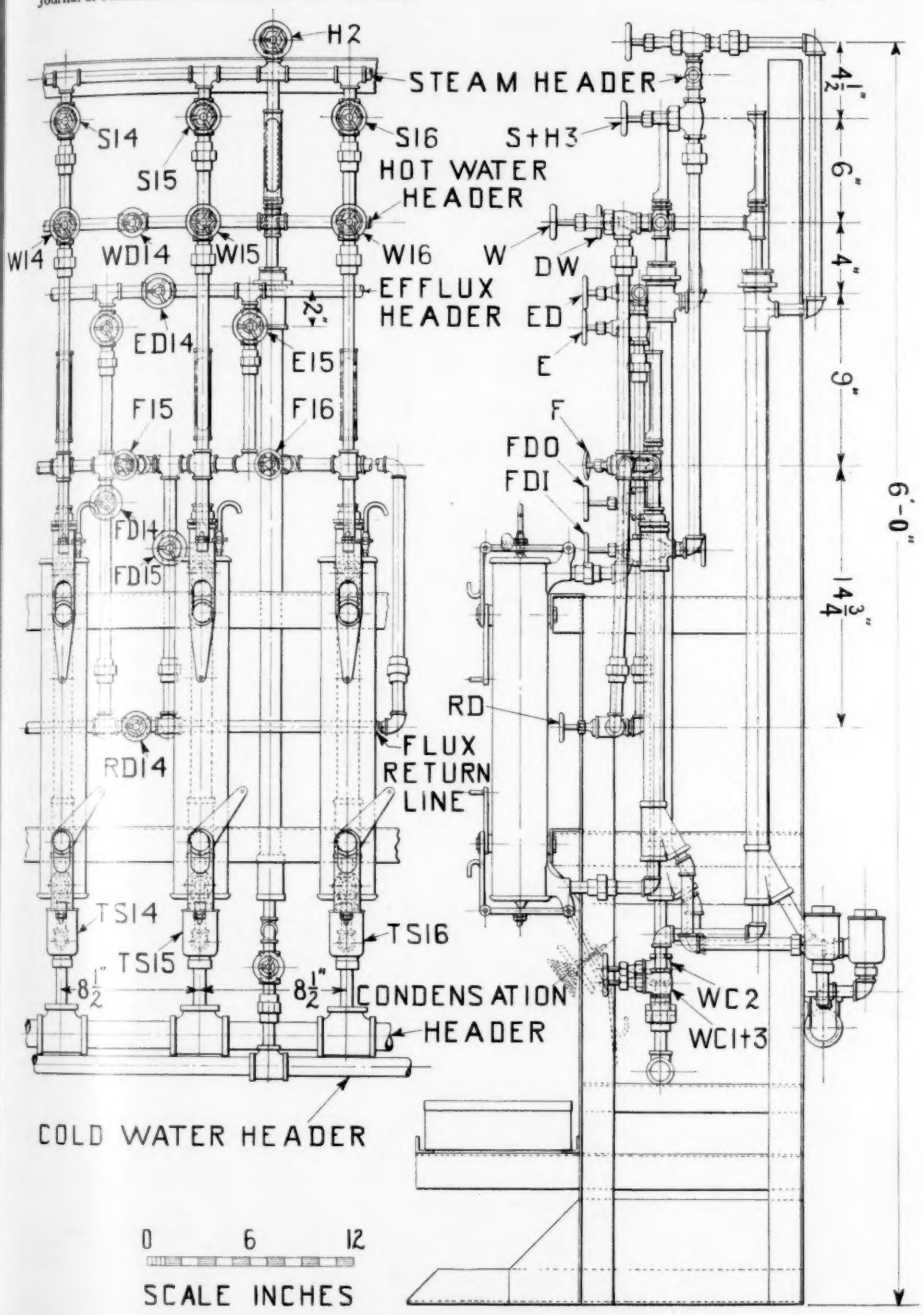


FIGURE 9.—*Straight battery assembly.*

(See appendix for explanatory text.)

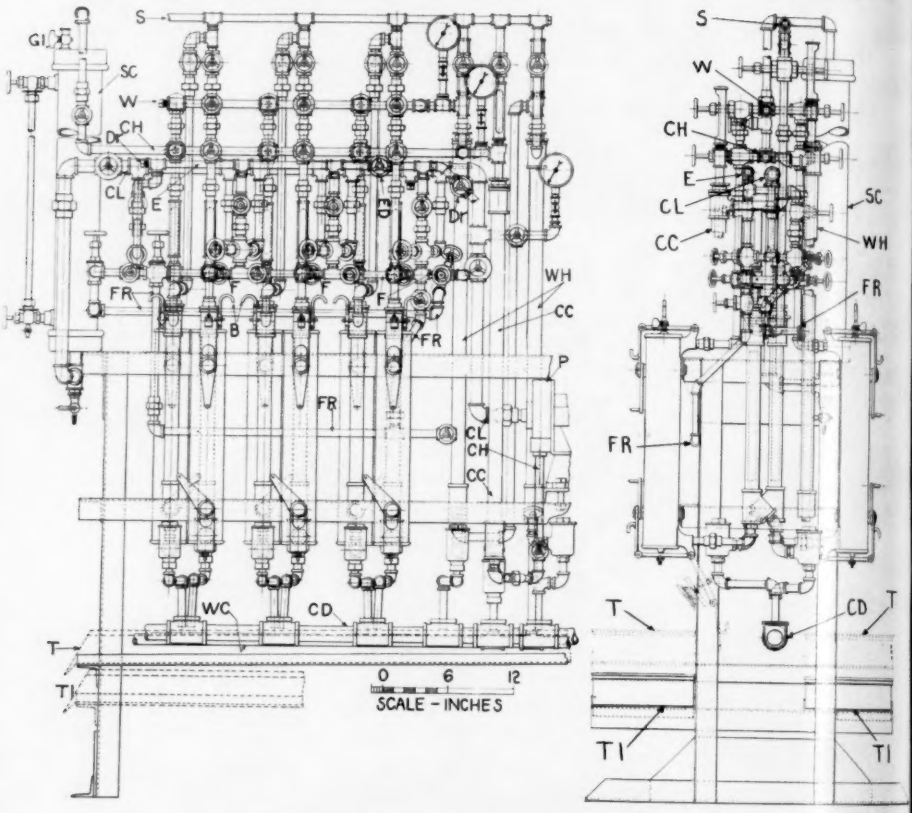


FIGURE 10.—*Folded-battery assembly.*

(See appendix for explanatory text.)

FIGURE 4.—*Flow diagrams with the circulatory system.*

At a the lower section of the column is being "preheated" by circulation of hot extract through the cells in parallel; at b, the same by circulation of the hot extract through the cells in series. Reagent dosage may be applied in the same way, with or without heating.

At c the circulatory system is being used to apply reagent dosage to the material at the middle of the column. Notice that in a and b, a section of the battery becomes a part of the circulatory system; while in c the circulatory system becomes, in effect, a unit of the battery placed directly in the course of the flux.

FIGURE 5.—*Diagram of pipe connections, per cell, (a) for the straight battery arrangement, and (b) for the folded battery arrangement with circulatory system.*

To bring out the fundamental simplicity of the connections in both cases, all the connections are placed in one plane and those pertaining to the middle cell are drawn in full lines. The relations of the contiguous cells in each case, and of the circulatory system also, in the folded arrangement, are indicated by broken lines.

The notation is as follows: E=efflux manifold; F_1, F_2, F_3=valve connections between flux and inlet manifolds; FM=flux manifold; IM=inlet manifold; C_H=high-pressure circulation manifold; C_L=low pressure circulation manifold; S_2, S_3=steam inlets to calorisators; X=valves which were not included in the experimental battery, but should be included if cell cut-out bridges are installed between flux manifolds, or if three tandem columns are to be operated on this installation with a separate efflux manifold for each column.

FIGURE 6.—*Cell body, cast brass.*

Construction and dimensions, with assembly view at left. Details of the attachments and fittings are indicated in figure 7, including special castings for constructing similar cells of standard brass tubing, which should yield cells of more uniform capacity.

Where uniform capacity is desired, however, it is suggested that the cast-brass cells be specified with machine finish inside, and with requisite tolerances as to variations in inside diameter and length. A=$\frac{1}{16}$-inch drill; B=$1\frac{9}{32}$-inch drill, $\frac{3}{8}$-inch—18NPT; C=$\frac{5}{16}$-inch drill, $\frac{3}{8}$-inch—16NC—2.

FIGURE 7.—*Cell attachments and fittings.*

Items 2 and 3. Special castings for bosses, when cells are constructed of brass tubing. Make 40 of thickness L and 40 of thickness M. Material: Brass. Finish: As indicated. Dimensions: H=$\frac{5}{16}$-inch drill, $\frac{1}{8}$-inch—16NC—2; I=1 inch; L=$\frac{1}{4}$ inch; M=$\frac{5}{16}$ inch; T=radius of O. D. of tubing.

Item 4. Pipe boss and cover bracket. Make 40. Material: Cast brass. Finish: As indicated. Dimensions: D=$\frac{3}{8}$ inch; E=$\frac{3}{16}$-inch drill; F=$1\frac{1}{2}$ inches; H=$1\frac{9}{32}$-inch drill, $\frac{3}{8}$-inch—18NPT; K=$1\frac{3}{8}$ to $1\frac{1}{2}$ inches; N=$\frac{5}{8}$ inch; radii as follows: T=O. D. of tubing; X=$1\frac{1}{4}$ inches; Y=$2\frac{1}{4}$ inches; Z=$1\frac{1}{4}$ inches; L=$1\frac{1}{2}$ inches.

Item 6. Yoke for doors and covers. Make 40. Material: Cast steel. Finish: Rough, except as indicated. Dimensions: A=$4\frac{13}{16}$ inches; B=$\frac{7}{16}$ inch; C=$1\frac{1}{2}$ inch, D=$\frac{3}{8}$ inch; E=$\frac{3}{8}$ inch; F=1 inch; H=$\frac{3}{16}$ inch; K=$\frac{5}{16}$ inch; N=$\frac{5}{8}$ inch; over-all length not to exceed $5\frac{1}{2}$ inches.

Item 8. Special toggle nut for securing door or cover to yoke. Make 40. Material: Steel. Finish: All over. Dimensions: E=no. 9 drill, $\frac{1}{4}$-inch—20NC—2; H=$\frac{1}{2}$ inch; radius of face curvature, $\frac{3}{8}$ inch.

Item 10. Doors and covers. Make 20 doors, 20 covers. Material: Cast brass. Finish: Rough, except as indicated. Dimensions: I=$2\frac{5}{8}$ inches; L=$3\frac{1}{4}$ inches; X=$3\frac{1}{2}$ inches; V=no. 9 drill, $\frac{1}{4}$-inch—20NC—2; U=80 to 82°; K=$\frac{3}{8}$ inch; N=$\frac{1}{8}$ inch; T=$\frac{3}{8}$ inch; Z=$\frac{3}{8}$-inch radius. For covers only: A=$\frac{1}{2}$ inch; E=$\frac{7}{8}$ inch; H=$2\frac{1}{64}$-inch drill, $\frac{1}{8}$-inch—27NPT; M=circle of 20-mesh brass wire cloth, $\frac{3}{4}$-inch diameter, cupped as indicated and soldered to cover as protection to pipe-tapped opening; $\frac{1}{4}$- by 2-inch flat-head machine screw in center opening, with head sweated into countersink to form water-tight joint. For (bottom) doors only: A=$\frac{3}{4}$ inch; strainer (item 15) sweated into countersink and $\frac{1}{4}$- by 2-inch steel machine screw sweated into strainer at one operation, to form water-tight joint.

Item 11. Jack-lock hasp. Make 40. Material: Cold-rolled steel or hard brass. Finish: Inside curve surface marked *f* to be polished; straight surfaces marked *f* to be machine finished. Dimensions: J, radius=0.500 to 0.501 inch; K, radius=0.75 inch; E=$\frac{3}{16}$ inch; F, radius=approximately $\frac{3}{8}$-inch, for finger hold; H=$\frac{3}{4}$ inch; L=$3\frac{27}{32}$ inches; N=$\frac{5}{8}$ inch; W=$1\frac{1}{2}$ inches; P=$\frac{1}{8}$ inch.

Item 12. Special shoulder bolt for jack-lock axle. Make 40. Material: Tool steel. Finish: All over, surface marked f to be polished. Dimensions: D=$\frac{3}{8}$-inch—16NC—3 min. number full threads, 4; I=$\frac{5}{16}$ inch; K, diam. of axle bearing, 0.495 to 0.490 inch; M, note that length of axle bearing is $\frac{1}{64}$ inch greater than thickness T of crank (item 13); N, thickness of washer-face of head=$\frac{1}{32}$ inch; V, thickness of hexagon head=$\frac{1}{4}$ inch.

Item 13. Jack-lock crank. Make 40. Material: Tool steel, one piece, except handle. Finish: All over, reamed hole and polished drum. Dimensions: E, hole $\frac{1}{8}$-inch eccentric; H, hole reamed to smooth surface, diam. $\frac{1}{2}$ inch±0.002; F, thickness and width of drum flange, one side only, as indicated, $\frac{1}{16}$ inch; J=diam. of drum, cylindrical surface polished, 1 inch; P, width of surface, $\frac{9}{64}$ inch; L=$3\frac{3}{4}$ inches; T=$2\frac{5}{64}$ inch; W=$1\frac{1}{2}$ inches.

Item 15. Strainer. Make 20. Material: Cast brass or bronze. Dimensions: E=$\frac{1}{4}$-inch drill; F=$1\frac{5}{16}$ inches; L=$2\frac{5}{8}$ inches; T=$\frac{3}{32}$ inch; U=80 to 82°; H=$\frac{1}{8}$ inch drill, 25/in.^{2} to $\frac{1}{4}$ inch from apex (at bottom as drawn).

Item 17. Gasket. Make 200. Material: Red rubber. Dimensions: H=$2\frac{5}{8}$ inches; E=$3\frac{1}{4}$ inches; T=$\frac{3}{32}$ inch.

Item 18. Gooseneck. Make 20. Material: Seamless drawn-copper tubing. Dimensions: E=$\frac{5}{16}$-inch O.D., $\frac{1}{32}$-inch wall; H=1 inch; F=$\frac{1}{2}$ inch; K=1°; to be silver-soldered to nipple of $\frac{1}{8}$-inch pet cock after turning latter to I.D. of tubing.

FIGURE 8.—*Heater, funnels, and troughs.*

Item 1. Heater assembly, as first constructed. Make 20 of 24-inch length and 3 of 36-inch length. Material: Inside duct of brass, $\frac{3}{8}$-inch iron pipe size; bottom fitting, standard $\frac{3}{8}$-inch brass elbow; D=$\frac{1}{2}$- by $1\frac{1}{2}$-inch brass nipple, threaded one end only, and reamed to O.D. of $\frac{3}{8}$-inch brass pipe, to which it is sweated with silver solder in the position indicated; H=$\frac{3}{4}$- by $\frac{3}{8}$- by $\frac{3}{8}$-inch brass tee; 2=expansion joint consisting of packed stuffing-box assembly, the component parts of which are presented in item 2; F=1- by 1- by $\frac{3}{8}$-inch galv. tee; E=1- by $\frac{1}{2}$- by $\frac{3}{8}$-inch galv. wye fitting, or 1-inch wye bushed to equivalent size. Dimensions: A=$4\frac{1}{2}$ inches; B=17 inches in the 24-inch calorisators applied to the cells, and 29 inches in the 36-inch water and juice heaters.

Item 2. Stuffing-box details. Twenty-three sets required, except as replaced by item 3 below. Material: Brass, either cast or turned from hexagon and round brass stock. Finish: As indicated. Dimensions: A=$1\frac{1}{2}$ inches; B=$\frac{3}{4}$ inch; C=$\frac{1}{4}$ inch; G, undercut, not wider than $\frac{1}{8}$ inch; D=$\frac{3}{8}$ inch; E=2 inches; F=$1\frac{3}{8}$ inches; H=0.68 inch (or slightly greater than O.D. of $\frac{3}{8}$-inch brass pipe); J, undercut, not wider than $\frac{1}{8}$ inch; K=$\frac{1}{4}$ inch; L=$1\frac{1}{8}$-inch p. d.—12—NS—2; P=1-inch—$11\frac{1}{2}$NPT.

Item 3. Cyclone. Alternate form of expansion joint used in later installations, one unit replacing D and E, and another unit replacing 2 and F, of the heater assembly. Forty-six required. Material: Cast iron. Finish: Rough, except as indicated. Dimensions: A, eccentricity of steam connection = 0.75 inch ± 0.03; B, length of ½-inch—14NPT = ½ inch; C = 1⅜ inches; D = 1½ inches; E, depth of stuffing box = ¾ inch; F, length of 1-inch—11½NPT = 9/16 inch; G = 23/32-inch drill, ½-inch—14NPT; H = 0.68 inch (or O. D. of ¾-inch brass pipe); I, length of cored race = 1 inch; J = 1⅝ inches; K, length exclusive of gland and stud bolts, not to exceed 2⅞ inches; L = 1 5/16 inches; M = 1-inch—11½NPT; N = no. 9 drill, ¼-inch—20NC—2; O = 5/16-inch drill; T, minimum thickness of stuffing-box bottom = 3/16 inch.

Item 4. Charging funnel. Three required. Materials: Skew cone, hard sheet brass of 0.35 to 0.52 mm thickness; plates and gate, ditto, approximately 1/16 inch in thickness; spreader bars between plates, about 0.025 inch thicker than gate; neck of seamless drawn-brass tubing, 2⅝ inches O.D., 0.065 to 0.049-inch wall-thickness. Dimensions: A = 2½ inches; D = 10½ inches; H = 8½ inches; E = 2⅜ inches; G = about 0.025 inch less than S; T = 3/8 to 7/16 inch; N = ½ to ¾ inch; turned-down portion of gate handle to form support even with neck of funnel, as indicated.

Item 5. Drip trough or troughs. One required for single-row straight-battery arrangement, two for folded-row arrangement. Material: Galvanized sheet iron for ordinary extractions, cold-rolled sheet brass for acid extractions; approximate thickness, 0.0375 inch. Dimensions: F, width of fold at top, ½ inch; E = 2½ inches; H = 1 inch; I = 30°; K = 45°; L, for straight battery = 15 feet 4½ inches; for folded battery, L = 9 feet 3½ inches.

FIGURE 9.—*Straight-battery assembly.*

End elevation and section of front elevation, indicating devices for dividing the battery between cells 14 and 15. Similar means was provided between cells 10 and 11. While the battery is divided at cells 14 and 15, valves WD14, ED14, RD14, and F15 are permanently closed, and valves FD14 and FD15 are operated in place of the valve F15.

Notation: Numerals following letters denote the cell (or heater) to which fitting is attached, or with which it is operated; S denotes steam valves; W, water (solvent) valves; E, efflux manifold valves; F, flux line stop valves; R, flux return line valves; D, a valve which is provided solely for dividing the battery; those marked O are for controlling the flow of flood liquid out of a cell by way of a flux return line; those marked I are for controlling the flow from the flux return line into the cell; valves admitting steam to a water heater are marked H2 and H3; valves marked WC control the flow of cold water into the water heaters 1, 2, and 3, respectively; and finally, TS denotes the steam traps.

FIGURE 10.—*Folded-battery assembly.*

End elevation and section of side elevation drawn as though representing a 6-cell battery instead of a 20-cell battery. One only (ED) of the valves required for dividing the battery into separate folded units is indicated. Notice that slight inconsistencies appear between the two elevations, which in the main, have been introduced for clarity of illustration. For example, the back flux return line is indicated at different levels in the two elevations; the circulation, efflux, and water manifolds are shown in section, and the valve ED, the cold-water main, and the circulation pump are omitted, in the end elevation; and parts of the water and circulation heaters are cut away in the end view.

Notation: B = air bleeders; CC = circulation manifold; CL = low-pressure manifold; Dr = draw-off connection; E = efflux manifold; ED = efflux manifold divider valve; F = flux line; FR = flux return line; GI = gas inlet to scrubber; P = circulation pump, with pedestal and driver and most of base broken away; S = steam manifold; SC = scrubber or saturator, with gage glass and draincock; T = position of drip trough as planned; TI = position of drip trough as installed, the lower position being more convenient for discharging the cells, especially into the sample receivers; W = hot water (solvent) manifold; WC = cold-water main; WH = two-pass water heater connecting cold-water main and hot-water manifold.

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THE DIFFERENCE IN VAPOR PRESSURES OF ORTHO- AND PARADEUTERIUM [1]

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ABSTRACT

The difference between the vapor pressures, $\Delta P(e\text{-}n)$, of the 20.4° K equilibrium mixture and the normal mixture of the ortho and para varieties of D_2 were determined from 15 to 20.4° K. $\Delta P(e\text{-}n)$ varied from 0.3 mm of Hg at 15° K to 3.8 mm at 20.4°. $\Delta P(e\text{-}n)$ for deuterium is small as compared with $\Delta P(e\text{-}n)$ hydrogen, but $[\Delta P(\text{ortho-para})/Pn]$ for deuterium is about equal to $[\Delta P(\text{para-ortho})/Pn]$ for hydrogen at the same temperature.

Further measurements were made on the uncatalyzed change with time of the vapor pressure of liquid normal deuterium. The change for deuterium is *less* than 1 mm of Hg in 200 hours, whereas the vapor pressure of liquid normal hydrogen increases 1 mm in 4 hours. This large difference in rates is attributable to the difference in magnetic moments of the proton and deuteron. If Wigner's theory of the ortho-para conversion by paramagnetic molecules in the gaseous phase is extended to the liquid phase to calculate the relative rates of change of the vapor pressures of liquid normal deuterium and liquid normal hydrogen, a ratio of 1/1000 is obtained for the ratio of the rate of change for deuterium to the rate of change for hydrogen.

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I. INTRODUCTION

The difference between the vapor pressures of ortho- and paradeuterium in relation to the corresponding difference for hydrogen is in itself interesting, but it also seems important because the physical basis of the vapor pressure difference, even for hydrogen, has not been made clear. Moreover vapor pressures of the ortho and para varieties have not been reported for any solid.

In table 1 are listed properties of molecular hydrogen and deuterium that are useful in the interpretation of the differences between

[1] The results contained in this paper were reported in part at the symposium on Heavy Hydrogen and Its Compounds, before a joint session of Section C of the American Association for the Advancement of Science and the American Physical Society, in Pittsburgh, December 28, 1934.

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the vapor pressures of ortho and para varieties of these isotopes. The arrows indicate the relative orientations of the spins of the protons and the deuterons, the spins being ½ and 1, respectively. The equilibrium concentrations of p-H_2 and o-D_2, the molecules with lowest rotational energy, $J=0$, increase as we proceed to lower temperatures.

TABLE 1.—*Concentration of ortho and para varieties of hydrogen and deuterium*

HYDROGEN	ORTHO	PARA
FERMI-DIRAC STATISTICS	↑ ↑	↑ ↓
J (ROTATIONAL QUANTUM NUMBER	ODD	EVEN
CONCENTRATION [1]		
at 300°K (n-H_2)	0.75	0.25
at 20°K (e-H_2)	0.002	0.998
DEUTERIUM	**ORTHO**	**PARA**
BOSE-EINSTEIN STATISTICS	↑ ↑ ↑ ↓	120°
J (ROTATIONAL QUANTUM NUMBER)	EVEN	ODD
CONCENTRATION [2]		
at 300°K (n-D_2)	0.667	0.333
at 20°K (e-D_2)	0.978	0.022

[1] Harkness and Deming, J. Am. Chem. Soc. **54**, 2850 (1932).
[2] Johnston and Long, J. Chem. Phys. **2**, 389 (1934).

The ortho-para deuterium vapor-pressure differences were calculated from the measured vapor pressures of the normal mixture, n-D_2, and the 20.4° K temperature equilibrium mixture, e-D_2. The e-D_2 mixture was established by means of a zinc chromite catalyst, $ZnCrO_2$, placed in the bottom of a vapor-pressure tube in which deuterium was condensed. The zinc chromite catalyst was prepared from zinc ammonium chromate, which was obtained by mixing equimolecular proportions of dilute solutions of zinc nitrate and ammonium chromate. The solution was made slightly alkaline with ammonia and the resulting precipitate washed, filtered, and dried. The product was heated for 5 hours at 450° C and was then reduced by hydrogen at 400° C for 24 hours. The final product was a pale-green powder which, by evacuation at 400° C, could be largely freed from traces of water which might interact with deuterium and thus contaminate it with hydrogen. Before use, it received a high-temperature treatment with deuterium to convert any residual water to deuterium oxide. Zinc chromite, thus prepared, is strongly para-

magnetic and has been found to be an excellent agent for conversion of o-H_2 to p-H_2 at liquid-air temperatures.[2] Although not so efficient as chromium oxide gel [3] in the conversion process, it is superior to the latter in the present work owing to its small residual water content.

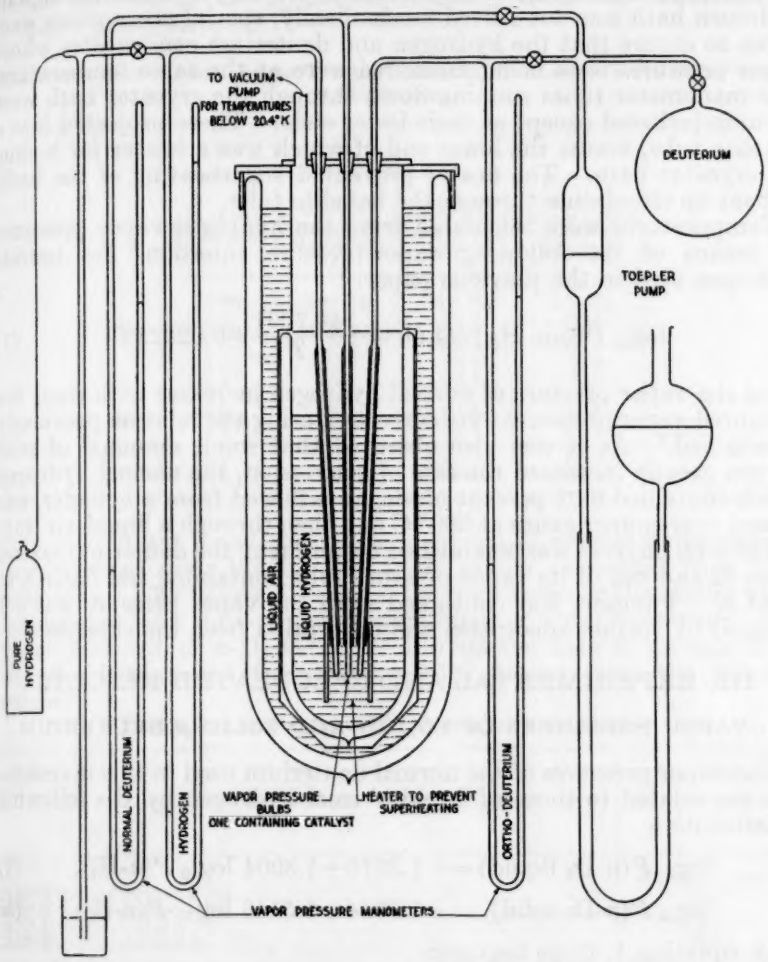

FIGURE 1.—*Apparatus used in the measurement of the vapor pressures of deuterium.*

II. DESCRIPTION OF APPARATUS

Figure 1 represents diagrammatically the apparatus used in making the vapor-pressure measurements. In a liquid-hydrogen cryostat were immersed three vapor-pressure tubes connected with oil-lubricated (n-butyl phthalate) mercury manometers. Normal hydrogen was condensed in one tube and normal deuterium in the other two, one of which contained the $ZnCrO_2$ catalyst.

[2] H. Diamond, Thesis, Princeton University (1935).
[3] Howard, Trans. Faraday Soc. **30**, 278 (1934).

The temperature of the liquid-hydrogen bath in the inner dewar vessel was varied by means of a vacuum pump. With the aid of a fine-adjustment valve and an oil-filled differential manometer it was possible to maintain the pressure in the vapor space over the liquid-hydrogen bath constant to ± 0.2 mm of mercury. Since the liquid-hydrogen bath was not stirred mechanically, special precautions were taken to ensure that the hydrogen and deuterium condensates whose vapor pressures were being measured were at the same temperature. The manometer tubes running down through the cryostat bath were vacuum-jacketed except at their lower ends. These projected into a bakelite tube, across the lower end of which was a heater for boiling the cryostat bath. The heater prevented superheating of the bath, and set up circulation through the bakelite tube.

Temperatures were calculated from the hydrogen vapor pressures by means of the following vapor-pressure equation [4] for normal hydrogen used in the previous paper: [5]

$$\log_{10} P(\text{mm Hg}) = 4.6633 - \frac{44.7291}{T} + 0.02023T \qquad (1)$$

Since the vapor pressure of normal hydrogen increases with time, the measured vapor pressures were corrected, using the relation previously determined.[6] As it was also observed that small amounts of solid oxygen greatly increased the rate of conversion, the normal hydrogen which contained 0.02 percent of air, as it flowed from a cylinder, was passed over copper gauze at 600° C and then through a liquid-air trap.

The e-D_2 mixture was established by pumping the deuterium several times in and out of its vapor-pressure tube containing the $ZnCrO_2$ at 20.4° K. Pumping was continued until the vapor pressure was not changed by further adsorption and desorption from the catalyst.

III. EXPERIMENTAL AND CALCULATED RESULTS

1. VAPOR PRESSURES OF LIQUID AND SOLID *n*-DEUTERIUM

The vapor pressures of the normal deuterium used in this investigation are related to those of liquid normal hydrogen by the following equations:

$$\log_{10} P(n\text{-}D_2 \text{ liquid}) = -1.3376 + 1.3004 \log_{10} P(n\text{-}H_2), \qquad (2)$$

$$\log_{10} P(n\text{-}D_2 \text{ solid}) = -1.9044 + 1.5143 \log_{10} P(n\text{-}H_2). \qquad (3)$$

With equation 1, these become:

$$\log_{10} P(n\text{-}D_2 \text{ liquid}) = 4.7266 - \frac{58.1657}{T} + 0.02630T, \qquad (4)$$

$$\log_{10} P(n\text{-}D_2 \text{ solid}) = 5.1572 - \frac{67.7333}{T} + 0.03063T. \qquad (5)$$

These equations represent the lowest vapor-pressure data yet obtained for deuterium and fit three of our samples prepared at different times.

[4] This equation was deduced as the best fit for the experimental data on (1) the vapor pressure of liquid hydrogen, (2) the latent heat of vaporization, and (3) deviations of the molecular volume of the vapor from that of an ideal gas. All published vapor-pressure measurements were considered, but this equation agrees best with the most recent Leiden measurements (van Agt and Onnes, Leiden Comm. no. 176b (1925)).

[5] Scott, Brickwedde, Urey, and Wahl, J. Chem. Phys. 2, 454 (1934).

[6] See footnote 5.

In table 2 are recorded two series of determinations of the vapor pressures of normal hydrogen and deuterium. The observed vapor pressures are given in columns 2 and 4. Column 3 is obtained from column 2 by correcting for the change (see footnote 5) with time of the vapor pressure of the hydrogen resulting from the conversion of ortho- to parahydrogen.

TABLE 2.—*Two typical series of observations of the vapor pressure of normal deuterium*

1	2	3	4
Age of condensed states	Observed vapor pressure of hydrogen	Vapor pressure of normal hydrogen (calculated)	Vapor pressure of normal deuterium (observed)
Hours	mm Hg	mm Hg	mm Hg
1.75	751.9	751.4	252.4
2.33	654.2	653.5	210.7
2.70	557.1	556.5	170.9
3.5	364.2	363.7	93.9
3.8	278.8	278.3	39.8
0.9	741.9	741.6	248.1
1.5	549.9	549.6	168.2
1.8	489.7	489.4	144.4
2.2	414.3	414.0	114.4
2.7	385.7	385.3	102.6

In table 3 are listed the vapor pressures of normal hydrogen and deuterium at their boiling and triple points calculated from these equations. The values differ slightly from those of the earlier paper because the later measurements were made of purer deuterium. The vapor pressure of n-D_2 at 20.38° K reported here is 1.3 mm lower and the triple-point temperature 0.13° higher than the previous values.[7]

TABLE 3.—*Calculated boiling points and triple points*

Temperatures	Vapor pressures	
	n-H_2	n-D_2
	mm Hg	mm Hg
23.59° K (boiling point of n-D_2)	1,753	760
20.38° K (boiling point of n-H_2)	760	256.2
18.71° K (triple point of n-D_2)	448	128.7
13.92° K (triple point of n-H_2)	54	5.2

2. VAPOR PRESSURE DIFFERENCES FOR NORMAL AND TEMPERATURE (20.4° K) EQUILIBRIUM DEUTERIUM

In table 4 are recorded observed differences between the vapor pressures of e-D_2 and n-D_2. These are plotted in figure 2.[8] The

[7] Scott, Brickwedde, Urey, and Wahl, J. Chem. Phys. **2**, 454 (1934).

[8] Figure 2 does not imply that the vapor pressures of the liquid and solid phases of e-D_2 at its triple point are not equal. At the high-temperature end of the lower-temperature curve is the triple point of e-D_2 and at the low-temperature end of the higher-temperature curve is the triple point of n-D_2. Between these two points the curve is continuous, but the interval between the triple-point temperatures (table 5) is too small to represent on figure 2.

Separate lines were drawn through the observations for the liquid and solid phases because there is no reason for a single line. The meeting of the lines of figure 2 would imply that e-D_2 and n-D_2 have the same triple-point temperatures. The ortho-para vapor-pressure difference of solid hydrogen has not been investigated, but e-H_2 has a lower triple-point temperature than n-H_2 (table 5). Therefore, the ΔP curve for hydrogen must be similar to that for deuterium (fig. 2).

measurements of series 1 and 2 were made on e-D_2 in a vapor-pressure tube without catalyst, after the D_2 had been converted to the equilibrium mixture in the tube containing the $ZnCrO_2$. The observations of the other series were made with e-D_2 in the presence of the catalyst. It was found that the presence of the $ZnCrO_2$ produced no appreciable change in the vapor pressure.

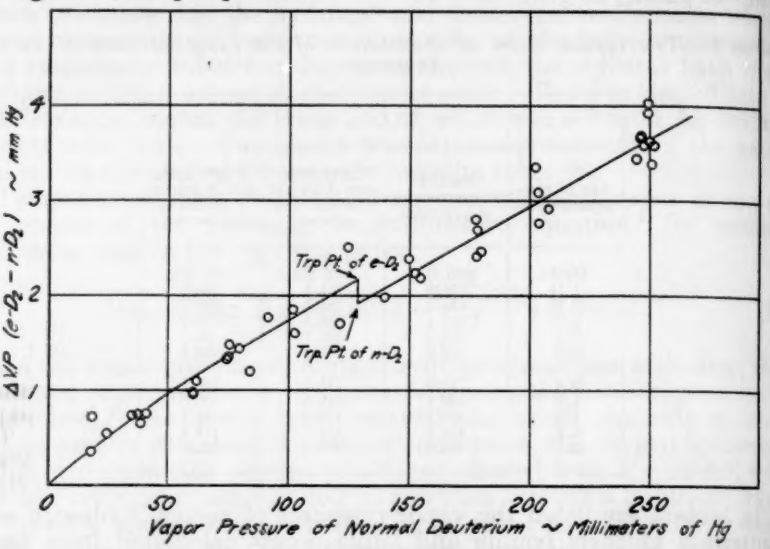

FIGURE 2.—*Vapor-pressure difference of 20.4° K temperature equilibrium deuterium (e-D_2) and normal deuterium (n-D_2).*

To prove that the observed ΔP's are to be attributed to a change in the ortho-para concentration and are not in error due to a contamination of the e-D_2 with hydrogen, the e-D_2 was pumped from its vapor-pressure tube into a flask in which it was converted to n-D_2 by a hot platinum filament, at the end of each day's observations, and the vapor pressure of the converted n-D_2 was compared the following day with a sample of unconverted n-D_2. The differences between the vapor pressures of the converted n-D_2 and the unconverted n-D_2 scattered to positive and negative values without any definite indication of a hydrogen contamination even after a second conversion to e-D_2 and reconversion to n-D_2.

TABLE 4.—*Experimental observations of $\Delta P(e\cdot D_2 - n\cdot D_2)$* (mm Hg)

December 13, 1934				December 14, 1934		December 15, 1934			
Series 1		Series 2		Series 3		Series 4		Series 5	
$(Pn\cdot D_2)$	ΔP	$P(n\cdot D_2)$	ΔP	$P(n\cdot D_2)$	ΔP	$P(n\cdot D_2)$	ΔP	$P(n\cdot D_2)$	ΔP
247.17	3.66	35.76	0.74	247.80	3.69	253.61	3.58	84.38	1.20
208.86	2.92	75.74	1.48	203.37	3.35	204.98	2.76	205.11	3.09
178.63	2.41	140.60	1.98	178.76	2.80	180.82	2.46	250.52	3.93
157.46	2.18	179.44	2.69	150.60	2.38	153.34	2.23	250.43	4.03
122.10	1.71	245.67	3.44	102.29	1.85	125.20	2.50	248.99	3.58
103.21	1.61	----------	----------	80.02	1.44	91.78	1.77	----------	------
75.56	1.36	----------	----------	60.58	0.97	74.60	1.33	----------	------
62.20	1.10	----------	----------	38.65	0.67	60.65	0.99	----------	------
37.77	0.76	----------	----------	18.08	0.37	41.18	0.76	----------	------
19.40	0.73	----------	----------	252.34	3.38	24.65	0.55	----------	------
----------	----------	----------	----------	251.56	3.62	----------	----------	----------	------

Although the D_2 used for this investigation probably was purer than any other previously used for vapor-pressure determinations, it may have contained a small but constant HD impurity. Since HD does not have ortho and para varieties, it should not have affected our results to any greater extent than in proportion to its concentration.

The vapor pressures of the 20.4° K equilibrium mixture of the ortho and para varieties of the deuterium used in this investigation are related to those of liquid normal hydrogen by the following equations:

$$\log_{10} P(e_{20.4}\text{°-D}_2 \text{ liquid}) = -1.3302+1.3000 \log_{10} P(n\text{-H}_2) \quad (6)$$

$$\log_{10} P(e_{20.4}\text{°-D}_2 \text{ solid}) = -1.8873+1.5106 \log_{10} P(n\text{-H}_2). \quad (7)$$

With equation 1, these become:

$$\log_{10} P(e_{20.4}\text{°-D}_2 \text{ liquid}) = 4.7321-\frac{58.1478}{T}+0.02630T \quad (8)$$

$$\log_{10} P(e_{20.4}\text{°-D}_2 \text{ solid}) = 5.1571-\frac{67.5678}{T}+0.03056T. \quad (9)$$

In table 5 are listed the triple-point temperatures and pressures of n-D_2, e-D_2, n-H_2, and e-H_2.

In table 6 values for deuterium, based on the curves of figure 2, are compared with corresponding values for hydrogen derived from the observations of Keesom, Bijl, and van der Horst.[9]

TABLE 5.—*Triple-point temperatures and pressures*

T and *P*	n-D_2	e-D_2	n-H_2	e-H_2[a]
Temperature, °K	18.71	18.67	13.92	13.79
Pressure, mm Hg	128.7	128.4	54	53

[a] Bonhoeffer and Harteck, Z. physik. Chem. [B] **4**, 113, (1929).

$\Delta P(o\text{-}D_2-p\text{-}D_2)$ and $\Delta P(p\text{-}H_2-o\text{-}H_2)$ were calculated from $\Delta P(e-n)$ on the assumption of Raoult's law. The smaller difference between the vapor pressures of e-D_2 and n-D_2 as compared with the corresponding difference for hydrogen is accounted for by the smaller percentage change in concentration and by a smaller difference between the vapor pressures of the ortho and para varieties. The difference between the vapor pressures of p-H_2 and o-H_2, $\Delta P(p\text{-}H_2-o\text{-}H_2)$, is about 3 times the corresponding difference $\Delta P(o\text{-}D_2-p\text{-}D_2)$ at 20.4° K and 5.7 times at 15° K. However, the ratio $\Delta P/P(n)$ is approximately the same for hydrogen and deuterium at the same temperature. (See table 6.)

[9] Roy. Acad. Sci., Amsterdam **34**, 1,223 (1931); also Leiden Comm. no. 217a.

TABLE 6.—*Comparison of ΔP's (mm Hg) for hydrogen and deuterium*

Temperature	Hydrogen				Deuterium			
	$P(n\text{-}H_2)$	$\Delta P(e\text{-}H_2 - n\text{-}H_2)$	$\Delta P(p\text{-}H_2 - o\text{-}H_2)$	$\frac{\Delta P(p\text{-}H_2 - n\text{-}H_2)}{P(n\text{-}H_2)}$	$P(n\text{-}D_2)$	$\Delta P(e\text{-}D_2 - n\text{-}D_2)$	$\Delta P(o\text{-}D_2 - p\text{-}D_2)$	$\frac{\Delta P(o\text{-}D_2 - p\text{-}D_2)}{P(n\text{-}D_2)}$
°K								
15	96.6	5.1	6.8	0.070	12.6	0.3	0.8	0.063
16	155.4	7.6	10.2	.066	25.9	0.5	1.7	.065
17	237.7	10.8	14.4	.061	49.4	0.9	2.9	.060
18	348.7	14.8	19.8	.057	83.2	1.6	4.9	.055
18.67 [a]	442.5	18.1	24.2	.055	126.5	2.2	6.7	.053
18.71 [b]	447.5	18.3	24.5	.055	128.7	1.9	6.2	.048
19	493.7	19.7	26.3	.053	146.3	2.2	6.9	.047
20	678.3	25.0	33.4	.049	221.0	3.2	10.4	.047
20.38	760.0	27.1	36.2	.048	256.2	3.8	12.1	.047

[a] Triple point of *e*-D_2.
[b] Triple point of *n*-D_2.

3. HEATS OF VAPORIZATION

As it is customary to use vapor-pressure data with the Clausius-Clapeyron equation to calculate latent heats, we have attempted to use our data to calculate the difference between the latent heats $\Delta L(n-e)$ of the normal and equilibrium mixtures of ortho and para varieties. In this calculation use was made of the following equation of state of hydrogen, which is very closely that used in the previous paper:

$$pV(\text{liters per mole})=RT-0.0381\left(1+\frac{1150}{T^2}\right)p \qquad (10)$$

In the absence of any data on the equation of state of deuterium at liquid-hydrogen temperatures, this same equation was used for deuterium as well. Substituting in the Clausius-Clapeyron equation for the volume of the saturated vapor from the above equation, the following relation for the difference between the latent heats $\Delta L(n-e)$ of the normal and equilibrium mixtures was obtained:

$$\Delta L(n-e)=R\frac{d\ln_e P_e/P_n}{d(1/T)}+T\left[v+0.0381\left(1+\frac{1150}{T^2}\right)\right]\frac{d\,P(e-n)}{dT} \qquad (11)$$

Here v is the molecular volume of the condensed state. For liquid hydrogen [10] it is 28.43 cm³, for solid deuterium [11] 23.15 cm³, and for liquid deuterium it was assumed to be 25.2 cm³ or 11.5 percent smaller than that of liquid hydrogen. For liquid hydrogen the *observations* of Keesom, Bijl, and van der Horst [12] were used. The two derivatives of equation 11 were determined graphically.

The results are tabulated in table 7 together with values of $\Delta L(p-o)$ calculated from $\Delta L(n-e)$ upon the assumption that ortho and para varieties form ideal solutions. The difference in signs of $\Delta L(p-o)$ for H_2 and D_2 arises from the interchange of the terms ortho and para to designate the rotating and nonrotating varieties of hydrogen and deuterium. The $\pm$ values are estimated probable errors.

TABLE 7.—*Differences between heats of vaporization*

Material	Temperature range	$L(n-e_{20.4°})$	$L(p-o)$
	°K		
Solid D_2	16 to 18.71	0.6 ± 0.5	1.8 ± 1.5
Liquid D_2	18.71 to 20.4	0.0 ± 0.5	0.0 ± 1.5
Liquid H_2	16 to 20.4	2.3 ± 0.5	-3.1 ± 0.7

It is interesting that $\Delta L(p-o)$ for liquid D_2 is not more nearly equal to $\Delta L(o-p)$ for liquid hydrogen.

The differences between the external latent heats of vaporization are small as compared with the values of table 7. Since $\Delta Pv(p-o)$ for the condensed phases is negligibly small, the ΔL values of table 7 are also the differences between the internal energies of the condensed states.

[10] Int. Crit. Tables **1**, 102 (1926).
[11] Clusius and Bartholomé, Z. tech. Physik **15**, 545 (1934).
[12] Proc. Amsterdam Acad. Sci. **34**, 1229 (1931).

4. ON THE UNCATALYZED CHANGE OF THE VAPOR PRESSURE OF LIQUID DEUTERIUM WITH TIME

Scott, Brickwedde, Urey, and Wahl [13] investigated the uncatalyzed change with time of the vapor pressures of liquid hydrogen and liquid deuterium resulting from the ortho-para conversion in the liquid state. The vapor pressure of normal hydrogen at 20.38° K increases at the rate of 1 mm of Hg in 4 hours, whereas the change for deuterium is less than 1 mm in 200 hours. The vapor pressure increase of liquid hydrogen follows the law of a bimolecular reaction, which Cremer and Polanyi [14] found to fit their thermal-conductivity measurements of the increase of p-H_2 in liquid hydrogen. Since the p-H_2 molecules have neither nuclear nor rotational magnetic moments, they have no magnetic field to effect a realignment of the nuclei of the ortho molecules with which they collide. Conversion in liquid hydrogen, therefore, results only from collisions of two ortho molecules. The o-H_2 molecules having a nuclear magnetic moment of 5.8 Bohr nuclear magnetons (BNM)[15] and a rotational magnetic moment of 0.85 BNM have resultant moments of 6.6, 5.9, and 5.0, averaging 5.8 BNM.

It is not to be expected that the conversion of p-D_2 to o-D_2 in liquid deuterium will follow the simple bimolecular change of hydrogen. Five-sixths of the o-D_2 molecules have a nuclear magnetic moment of 1.5 BNM [16] and the remaining sixth has a zero moment; there is no rotational moment. The p-D_2 molecules have a nuclear magnetic moment of 0.75 and a rotational moment of 0.42 BNM.[17] The resultant moments of p-D_2 are 1.2, 0.9, and 0.3, averaging 0.8 BNM. It is seen, therefore, that not only does the para- to orthodeuterium conversion result from collisions of para and ortho molecules as well as collisions of para molecules, with each other, but that actually the para-ortho collisions are more effective since the magnetic moments of the ortho molecules are greater than those of para molecules.

Wigner [18] developed a theory for the ortho-para conversion in gaseous hydrogen resulting from collisions with paramagnetic oxygen molecules. This theory is not directly applicable to liquids, but it does seem justifiable to use it to calculate the order of magnitude of the relative rates of conversion in liquid hydrogen and deuterium.

For the ortho to para conversion in gaseous hydrogen resulting from collisions with paramagnetic oxygen, the probability, W, of a transition from $J=1$ to $J=0$ is related to the moment of inertia I_H of the H_2 molecules, the magnetic moments μ_1 and μ_2 of the oxygen molecule and the proton, and the spin, i, of the proton. We apply this relation to the ortho to para conversion

$$W(J=1\rightarrow J=0)\propto I_H\mu_1^2\mu_2^2\left(\frac{2i+1}{i}\right) \tag{12}$$

resulting from collisions with paramagnetic o-H_2 in liquid H_2, substituting for μ_1, the magnetic moment of o-H_2. The velocity constant,

[13] Scott, Brickwedde, Urey, and Wahl, J. Chem. Phys. **2**, 454 (1934).
[14] Z. physik. Chem. [B] **12**, 231 (1921).
[15] I. Estermann and O. Stern, Nature **132**, 169 (1933); **133**, 911 (1934). I. I. Rabi, J. M. B. Kellogg, and J. R. Zacharias, Phys. Rev. **46**, 157 and 163 (1934).
[16] See footnote 15.
[17] The value 0.42 is based upon the assumption that the rotational moments are proportional to the angular velocities of rotation.
[18] Z. physik. Chem. [B] **23**, 31 (1933).

K_H, of the ortho to para conversion in liquid hydrogen is proportional to $W(J=1\rightarrow J=0)$. Substituting numerical values for the symbols in equation 12, we obtain:

$$K_H = CI_H\left[\frac{(6.6)^2+(5.9)^2+(5.0)^2}{3}\right](2.9)^2 4 = 1.2\times 10^3 C'.$$

For the para to ortho conversion in liquid deuterium resulting from the collision of two para molecules

$$W_{p,p}(J=1\rightarrow J=0) \propto I_D \mu_1^2 \mu_2^2 \frac{(i+1)(2i+1)}{i^2}. \tag{13}$$

The different statistics applicable to H and D require different spin factors in equations 12 and 13.

$$K_{p,p} = C(2I_H)\left[\frac{(1.2)^2+(0.9)^2+(0.3)^2}{3}\right](0.75)^2 6 = 5.3C'.$$

For the para to ortho conversion resulting from collisions of o-D_2 and p-D_2 molecules

$$W_{o,p}(J=1\rightarrow J=0) \propto \frac{5}{6}\times\frac{1}{2} I_D \mu_1^2 \mu_2^2 \frac{(i+1)(2i+1)}{i^2} \tag{14}$$

and

$$K_{o,p} = C\times\frac{5}{12}(2I_H)(1.5)^2(0.75)^2 6 = 6.3C'.$$

The factors $\frac{5}{6}$ and $\frac{1}{2}$ were introduced to take account of the fact that (1) only $\frac{5}{6}$ of the o-D_2 molecules have a magnetic moment, and (2) the *a priori* probability of a para to ortho conversion for the collision of an ortho and a para molecule is only half of that for the collision of two para molecules.

If $[o\text{-}H_2]$ and $[p\text{-}D_2]$ are the concentrations of o-H_2 and p-D_2 in liquid hydrogen and liquid deuterium, respectively,

$$\frac{\text{-}H_2]}{dt} = K_H[o\text{-}H_2]^2 = 1.2\times 10^3 C'[o\text{-}H_2]^2$$

and

$$\frac{d[p\text{-}D_2]}{dt} = K_{p,p}[p\text{-}D_2]^2 + K_{o,p}(1-[p\text{-}D_2])[p\text{-}D_2]$$
$$= \{6.3[p\text{-}D_2] - [p\text{-}D_2]^2\}C'.$$

The ratio of the rate of o-$H_2\rightarrow p$-H_2 in liquid normal hydrogen, to the rate of p-$D_2\rightarrow o$-D_2 in normal deuterium is

$$\left(\frac{d[o\text{-}H_2]}{dt}\right)_{n\text{-}H_2} \Big/ \left(\frac{d[p\text{-}D_2]}{dt}\right)_{n\text{-}D_2} = 3.4\times 10^2.$$

For the ratio of the rates of change of the vapor pressures we have:

$$\left(\frac{dP}{dt}\right)_{n\text{-}H_2} \Big/ \left(\frac{dP}{dt}\right)_{n\text{-}D_2} = 1\times 10^3.$$

Although this calculation is not to be regarded as rigorous, it shows that the rate of conversion of para- to orthodeuterium is approximately proportional to the concentration of p-D_2 instead of to the square of the concentration as it is for the corresponding change in liquid hydrogen. It also shows that the rate of the para to ortho conversion in liquid deuterium must be very much smaller than for the ortho to para conversion in liquid hydrogen.

Figure 3 (A and B) are graphs of observations of the vapor pressure of normal deuterium at 20.38° K plotted against the age of the condensed state. Figure 3 (A) is a reproduction of previously reported data obtained February 1934. The data of figure 3 (B) were observed December 1934, using purer deuterium. ΔP is the difference between the observed vapor pressure and the intercept with the axis of vapor pressures of a line through the observations determined by

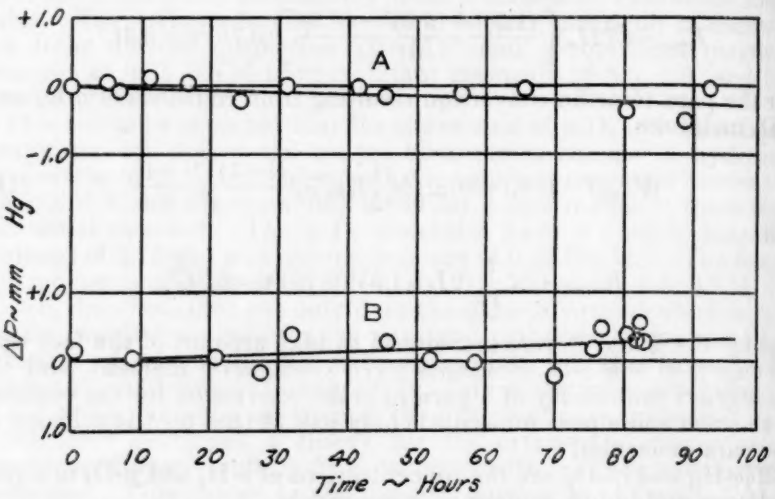

FIGURE 3.—*Uncatalyzed change in the vapor pressure of liquid normal deuterium at 20.4° K.*

A. Observations of February 1934.
B. Observations of December 1934.

the method of least squares, with each point given equal weight.[19] These are the lines drawn through the observations in the two figures. The observations of February indicate a slow decrease in vapor pressure with time, whereas those of December indicate an increase about equal to the decrease of the February observations. When the two series of observations are thrown together and treated statistically as a single set, the line through the observations, determined by the method of least squares, indicates a decrease in vapor pressure of 0.027 mm of Hg in 100 hours. We conclude that the vapor pressure of liquid normal deuterium over a period of 100 hours is constant to within the accuracy of our measurements. The *estimated probable error* calculated from our observations is ± 0.27 mm at 100 hours.

[19] We are indebted to W. E. and L. S. Deming of the Bureau of Chemistry and Soils, U. S. Department of Agriculture, for the statistical analysis of our data.

IV. ROTATION IN THE CONDENSED STATES

Although it was surmised that there would be *free* rotation of deuterium molecules in the liquid and solid states just as in the case of hydrogen, we now have definite evidence from the ortho-para vapor pressures that this is so. The latent heats of vaporization of solid and liquid deuterium are 355 and 305 calories per mole, respectively, and the rotational energy ($J=1$) of p-D_2 in the vapor phase at liquid-hydrogen temperatures is 170 calories per mole.[20] If there were no rotation in the condensed states, the heats of vaporization of p-D_2 would be about 170 calories per mole greater than the corresponding values for o-D_2. Actually there may be a small difference in the heats of vaporization of p-D_2 and o-D_2, but it is less than for liquid hydrogen, in which the difference is 3 calories per mole. We conclude, therefore, that there is free rotation in condensed states of deuterium just as in the case of hydrogen.

WASHINGTON, August 13, 1935.

[20] Johnston and Long, J. Chem. Phys. **2**, 389 (1934).

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THE WAIDNER-WOLFF AND OTHER ADJUSTABLE ELECTRICAL-RESISTANCE ELEMENTS

By E. F. Mueller and Frank Wenner

ABSTRACT

The Waidner-Wolff adjustable resistance element has to a considerable extent been used in resistance-measuring apparatus and potentiometers. It serves to change the resistance of a circuit in a number of small and equal steps by means of a dial switch, at the same time reducing the effect of variations of resistance of the switch contacts and thermoelectromotive forces in the switch. The Waidner-Wolff element, modifications of it, and another arrangement serving substantially the same purpose are considered in some detail. A three-terminal element used in bridge circuits and a four-terminal parallel element are also described. The adaptability of the parallel element to form useful combinations with similar or different elements is illustrated by examples. Finally, there is a list of the more important adjustable resistance elements now available to the designer of apparatus.

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I. INTRODUCTION

From time to time, since the organization of the National Bureau of Standards in 1901, occasions have arisen requiring the use of a combination of electrical resistors the resistance of which may be changed over a limited range in a large number of equal steps of desired magnitude. These changes might be made by the use of a suitable number of dial switches with contacts directly in the circuit, as in the ordinary dial resistance box. However, in many cases, variations of the resistances of the switch contacts are larger than is permissible in the resistor, or even larger than one of the steps. Also, in many cases, the thermoelectromotive forces in the switches are larger than is permissible in the resistor. Both of these difficulties have been obviated or materially reduced by placing the switch contacts in a shunt having a resistance several times that of the resistance of that part of the resistor shunted. Since each dial switch and the resistance

sections directly associated with it may be considered more or less independently of the others, each will be referred to as an adjustable resistance element. While some of the arrangements used or proposed have been described elsewhere, others have not been described or the descriptions are not sufficiently complete to give a definite understanding of their advantages and limitations. It is the purpose of this paper to give a connected discussion of the different adjustable resistance elements developed in this Bureau as well as to provide a list of the more important ones now available for use in design of resistance apparatus.

II. THE WAIDNER-WOLFF ELEMENT

The Waidner-Wolff resistance element or decade was devised at the National Bureau of Standards about 1902 by C. W. Waidner and F. A. Wolff. It consists essentially of a relatively small fixed resistance shunted by another larger resistance, the latter variable by means of a dial switch, in 10 unequal steps, so chosen that the resultant resistance is variable in 10 equal steps, and for the highest step the resistance of the shunt is infinite.

One of the advantages of the element is that the values of the resultant equal resistance steps depend upon the values of comparatively large resistances which need be adjusted to an accuracy only slightly higher proportionally than that desired for the resistance steps. As the switch is in a shunt circuit of relatively high resistance, variations of the resistance of switch contacts, or electromotive forces originating in the switch, produce only a small fraction of the effect that they would produce if the switch were directly in the main circuit. Thus it is possible to have a decade with definite steps, even when the ordinary variations in the contact resistance of the switch are larger than the steps themselves. A disadvantage is that the resistance of the element cannot be reduced to zero.

In one of the original applications, three such elements in series, providing steps of 0.001, 0.0001, and 0.000 01 ohm, respectively, were used as a substitute for the slide wire previously used in the Callendar-Griffiths bridge for resistance thermometry, as described by Griffiths (see bibliography for references). In another application, four elements, the smallest with steps of 0.000 001 ohm, were used in one of the two ratio arms of a Wheatstone bridge or a Thomson double bridge. Apparatus embodying both of these applications was delivered to this Bureau in 1903.

The element has since been used to a considerable extent in resistance-measuring apparatus and potentiometers. It was first described very briefly by Waidner and Dickinson. It was described in detail by White as a well-known device of presumably remote origin, and has been mistakenly attributed to him by several writers, although he explained its origin in a later publication.

The element is illustrated in figure 1, in which the sketch marked "A" represents the element with the customary marking when it is connected to provide 10 resistance increments of 0.01 ohm each. The sketch marked "B" shows the notation to be used in the subsequent discussion. The reason why this notation is preferred for purposes of calculation will become self-evident in connection with the calculations for the modified Waidner-Wolff element. In some applications, the element would actually be marked as shown in

sketch B. When two or more elements are used in series, the marking X is preferred to the marking 10, because X may be recorded as if it were a digit, and this has several advantages.

The fixed resistance of the element is represented by r, which is a four-terminal conductor, so that the resistance included in it is definitely fixed by the positions of the branch points. When the switch is on the 0 position of figure 1 B, the resistance of the element is r. For the switch positions 1, 2, etc., the corresponding resistance of the entire shunt, including connecting resistances and switch contacts, is designated as S_1, S_2, etc. If the connecting and contact resistances omitted are exactly equal to those introduced when the switch is moved, for example from 3 to 4, then S_3-S_4 is equal to ${}_3A_4$. According to the notation used here, ${}_3A_4$ designates the drop in potential from 2 to 4 divided by the current in the shunt with the switch on position 3. It will be convenient to speak of the difference between the resistance of r and the combination of r shunted by S, as the "lowering", L. Thus L_0, L_1, L_2, etc., are the lowerings corresponding to switch positions 0, 1, 2, etc. Since the shunt S_0 is infinite, $L_0=0$. Since all the steps are equal, each step is also equal

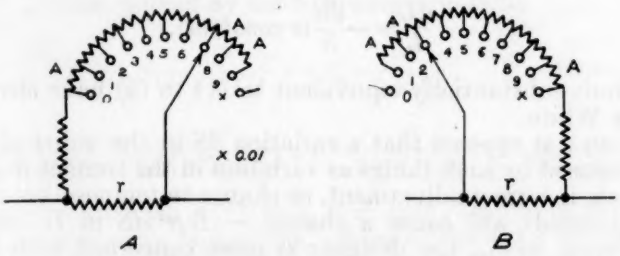

FIGURE 1.—*Waidner-Wolff element*

A. Element with customary marking for 10 resistance increments of 0.01 ohm each.
B. Element marked to show notation used in discussion and calculations, illustrative of lowerings in ten equal steps.

to L_1. The resistance of a circuit which includes the element shown in figure 1 cannot be reduced below $r-10L_1$.

In designs in which this element has been used, the individual steps have been made as large as 0.1 ohm, and as small as 0.000 001 ohm. Elements with steps larger than 0.1 ohm require a higher minimum resistance than is permissible in many designs, while none with steps smaller than 0.000 001 ohm have as yet been used.

Where this element is included in an instrument, the user may have no knowledge of the existence or magnitude of r, since all he observes directly is that when the switch is moved from any position to an adjacent one the resistance of the resistor changes by L_1. The characteristics of the element can also be described in an especially simple form by making use of the "lowering" L.

If S, without subscript, denotes the resistance of the shunt for any position of the switch, the corresponding value of L is given by the expression

$$L=\frac{r^2}{r+S} \qquad (1)$$

Differentiating (1) with r constant and simplifying

$$dL=-\frac{L^2}{r^2}dS. \tag{2}$$

If an electromotive force, E, originates in S, the resulting potential drop, e, between the terminals of the element is

$$e=\frac{L}{r}E. \tag{3}$$

If the element is part of a more extended circuit, the potential drop across its terminals will be smaller than e in eq 3.

No approximations are involved in the above relations, so that they are applicable to any two resistors in parallel.

If r is small compared with S, then approximately

$$\frac{dL}{L}=\frac{2dr}{r}\ (S\ constant), \tag{4}$$

and

$$\frac{dL}{L}=-\frac{dS}{S}\ (r\ constant). \tag{5}$$

Relations substantially equivalent to (1) to (5) have already been given by White.

From eq 2 it appears that a variation dS in the value of S, which may be caused by such things as variation in the contact resistance of the switch, incorrect adjustment, or change in temperature (r remaining unchanged) will cause a change $-(L^2/r^2)dS$ in L. Since L is largest when $S=S_x$, the designer is most concerned with this case, and unless otherwise specified in the subsequent discussion, consideration will be limited to this case. If L_x is fixed, as it is, for example, in an element having 10 steps of 0.01 ohm each, then $\frac{L_x^2}{r^2}$ varies inversely as r^2, so that it is doubly advantageous to make r as large as permissible for a given value of L_x, up to the point where the effect of variation of contact resistance becomes negligible. In elements actually used, with one exception (example 5 of table 1) L_x/r has not exceeded 1/7 so that in the most unfavorable case, dL was only about $dS/50$. Equation 2 is a special case of a general relation:

$$dR=(i_a/i)^2da$$

where R is the resistance of a network, a is the resistance of one of the branches, and i_a/i is the ratio of the current in the branch to the current in the network.

From eq 3 it follows that if $L/r=1/7$, e will be equal to (or somewhat less than) $E/7$, so that the element is inherently more effective in reducing the effect of variations of the resistance of switch contacts than it is in reducing the effect of electromotive forces originating in the switch.

From eq 4 it appears that r must be adjusted with twice the proportionate accuracy required for L_x, assuming that S_x is correctly adjusted, and from eq 5 that any S must be adjusted to the same

proportionate accuracy as is required for the corresponding L, assuming r correctly adjusted. Each "A" section must be adjusted to the proportionate accuracy desired for the step to which it corresponds.

If only one element is to be included in a design, the choice of the value of r is limited by two considerations. One of these is that L_x^2/r^2 or L_x/r shall not exceed some value determined by the requirements of the design and the quality of the switch to be used, and the other is that $r-10L_1$ shall not exceed a value determined by the requirements of the design. Within the range permitted by these considerations there is usually a wide latitude for choice.

In many cases, two or more elements in series are used in a circuit, the steps of the second being 0.1 those of the first, those of the third 0.1 those of the second, etc. Such combinations will be called successive elements. Where two or more successive elements are used in one circuit, the total permissible resistance should be suitably apportioned among them. In the following discussion such considerations as simplicity in manufacture, and appropriate distribution of the permissible resistance among several successive elements will be shown to afford useful criteria for selecting values for the shunted resistances.

The values of the resistances S_0, S_1 ---------- S_x and of ${}_1A_2$, ${}_2A_3$ ---- ${}_9A_x$ are defined by the following equations

$$r+S_0=\frac{r^2}{0\times L_1};\quad r+S_1=\frac{r^2}{1\times L_1};\quad r+S_2=\frac{r^2}{2\times L_1}\quad \text{----}\quad r+S_x=\frac{r^2}{10\times L_1} \tag{6}$$

$${}_0A_1=\frac{r^2}{0\times 1\times L_1};\quad {}_1A_2=\frac{r^2}{1\times 2\times L_1};\quad {}_2A_3=\frac{r^2}{2\times 3\times L_1}\quad \text{----}\quad {}_9A_x=\frac{r^2}{9\times 10\times L_1}. \tag{7}$$

It is apparent from eq 7 that if r^2 and L_1 both be multiplied or divided by the same factor, the values of the "A" sections will be unchanged. Thus one set of values for the "A" coils may be used for two or more successive elements if appropriate values are assigned to r and S_x in each case.

In eq 7 all the numbers from 1 to 10 appear in the denominators. Consequently if r^2 in the numerator contains the factors 7 and 9, the values of the "A" coils will have no recurring decimals. This suggests making $r^2=.63n$, where n is a number, not necessarily an integer, which is best characterized as one to be chosen with discretion. The position of the decimal point in the number so chosen for r^2 may be shifted as desired to produce appropriate values for L_1 and the "A" coils. By giving n a series of values such as 1.6, 2, 2.4, 3, 4, 5, 6, 8, 10, 12, 16, 20 --- 160, a series of 21 values of r is obtained, each about 12 percent larger than the one preceding, the first being 1.004 ohms and the last 10.04 ohms. From this series, a value of r differing at most by 6 or 8 percent from a desired value may be selected. If, for example, an element with 0.1-ohm steps is required, in which L_x/r is not to exceed 1/7, n may be taken equal to 80, so that $r^2=50.4$, $r=7.1$, $S_x=43.3$ and the nine "A" coils beginning with ${}_9A_x$ have values of 5.6, 7, 9, 12, 16.8, 25.2, 42, 84, 252, and ∞ ohms. The values given for r and S_x are correct within 1 in 10 000, those for the "A" coils are exact.

A second series similar to the one above can be derived by multiplying each n by 4 and shifting decimal points as required, giving the new n the values 1.6, 2.0, 2.4, 3.2, 4.0, 4.8, 6.4, 8.0, 9.6, 12, 16, etc. Many

other such series can be made, but the two given contain most of the more useful combinations.

Elements of the type described have been preferred in several instances in the design of apparatus, because of the resulting simplification in manufacture. Examples of some sets of successive elements that have been used or proposed are shown in table 1, in which values of r^2 and n are tabulated. The column headed "minimum Σ" represents the sum of the resistances of the elements when the shunts have their lowest values, corresponding in the usual case to all switches in the zero positions. The column $\Sigma L^2_x/r^2$ shows, in the case of example 1, that the effect of variations in the three switch contacts is 1/4500 of the effect of a single switch directly in the circuit, and similarly, the column of $\Sigma L/r$ shows that the effects of electromotive forces at the three switch contacts is 1/50 of the effect for a single switch directly in the circuit.

In examples 1 to 6, the corresponding "A" sections of the several elements in each example are the same. Examples 7 to 9 will be mentioned later.

TABLE 1.—*Examples of successive elements*

Tabulated values in columns 2 to 6, inclusive, are those of r^2, and n (in parentheses)

Example	Steps (ohms) (L_1)					Minimum Σ (ohms)	$\Sigma L_x^2/r^2$	$\Sigma L_x/r$
	0.1	0.01	0.001	0.0001	0.000 01			
1			.504 (.8)	.0504 (.08)	.00504 (.008)	.994	1/4500	1/50
2		1.26 (2)	.126 (.2)	.0126 (.02)		1.48	1/114	1/8
3			1.26 (2)	.126 (.2)		1.47	1/11600	1/86
4		.6048 (.96)	.06048 (.096)	.006048 (.0096)		.991	1/54	1/5.2
5	12.6 (20)	1.26 (2)	.126 (.2)	.0126 (.02)		4.03	1/11.4	1/2.5
6	50.4 (80)	5.04 (8)	.504 (.8)	.0504 (.08)		9.16	1/45	1/5
7	75.6 (120)	2.52 (4)	.252 (.4)	.0252 (.04)		9.83	1/57	1/5
8	100	1	.01	.0001		10.00	1/25	1/2.5
9	35.2	8.80	2.20	.55		10.00	1/34	1/4.8

While sets of elements of the type illustrated in examples 1 to 6, table 1, have the advantage of simplifying construction and have been found satisfactory in service, it is of interest to determine whether this distribution of resistance among the elements is advantageous in other respects.

In two successive elements of this kind, the value of L_x^2/r^2 in the lower one is 1/10 and the value of L_x/r is $1/\sqrt{10}$ times that in the higher one. Thus in four successive elements the value of L_x^2/r^2 in the lowest is 0.001 and the value of L_x/r is about 0.03 of that in the highest one. This suggests the possibility that the aggregate effects for the four elements might be appreciably reduced by a redistribution of resistance among them, subject to the condition that the sum of the shunted coils remain fixed.

It can be shown that for any number of successive elements having shunted resistances r_a, r_b --- etc., and subject to the condition that Σr is a constant, the aggregate value of L_x^2/r^2 will be a minimum if the values of r form a geometric progression with $r_a=\sqrt[3]{100}r_b=\sqrt[3]{100^2}r_c$ etc., and the aggregate value of L_x/r will be a minimum if $r_a=\sqrt{10}r_b=10r_c$, etc.

Examples 6, 7, 8, and 9 of table 1 represent combinations of four elements in each of which the minimum Σ is about 10 ohms. In

example 8, L_x/r is the same for each element. Examples 6 and 7 represent approaches to minimum values for $\Sigma L_x/r$ and $\Sigma L_x^2/r^2$, while in example 8 the ratio of successive values of r is greater, and in example 9 the ratio is less than that required for a minimum in either case. It is apparent that even the rather large departures from the condition for minimum effects involve no serious sacrifice in performance.

Furthermore, it does not follow that the combinations with the minimum values will necessarily be the optimum combinations. A selection of values involves a consideration of the purposes for which the apparatus is to be used, and in general can be made only between more or less indefinite limits. Combinations like those in the first six examples of the table 1 usually will be found to be sufficiently near optimum to make their use advantageous.

In all the elements of examples 1 to 7 of table 1, the values of r and S_x are incommensurable numbers. It is possible to make an element in which no incommensurable numbers or recurring decimals occur, by making $r=.21n$. Such elements are not, however, as useful as the elements illustrated in examples 1 to 7 of table 1.

The combination shown in example 1 of table 1 is substantially the same as that mentioned by Waidner and Dickinson, although the values of r in their combination were slightly different, so that corresponding "A" coils were not equal. The combination of example 2 has been used in several hundred resistance-thermometer bridges.

III. MODIFICATIONS OF THE WAIDNER-WOLFF ELEMENT

The above discussion applies to the arrangement devised by Waidner and Wolff, and used in most of the resistance-thermometer bridges constructed in accordance with designs developed at this Bureau, in some potentiometers developed elsewhere, and in some of the apparatus formerly used in the testing of precision resistance standards. In all of the above discussion there has been an implicit assumption that the resistance introduced into a circuit by use of the elements with the dials set on lowest readings must be kept low. In this case it is advantageous to use the Waidner-Wolff arrangement in which the shunt on the highest reading is infinite. However, in many cases, the resistance is not severely limited, or the effect of contact resistance or thermal emf need not be reduced to the limit possible for a given resistance. Under these circumstances the Waidner-Wolff element may be modified by making the resistance of the shunt corresponding to the X or highest reading of the dial switch, of moderate instead of infinite value. This modification was first used by one of the authors (Wenner) about 1912.

In calculating resistance values for elements of this type, an extension of eq 6 and 7 may be used. Referring to figure 1 B, the lowering need not be limited to the range from $0L_1$ to $10L_1$ but may be from nL_1 to $(m+n)\ L_1$ where, in practical instances, values of n range from 0 to more than 10 000. In the original Waidner-Wolff element, n is 0. Furthermore in some cases n is not an integer, though m is an integer equal to the number of steps of the element. Consider for example that r is 60 ohms and the resistance of the element is to be adjustable from 49.5 to 50.5 ohms in steps of 0.1 ohm. Since the

steps are 0.1 ohm, L_1 is 0.1 ohm, and the lowering, L, from 60 to 50.5 ohms is $95L_1$ (or n is 95). Therefore from eq 7 it follows that

$$_{95}A_{96}=\frac{3600}{95\times96\times0.1};\ _{96}A_{97}=\frac{3600}{96\times97\times0.1};\ \text{---};\ _{104}A_{105}=\frac{3600}{104\times105\times0.1}$$

while from eq 6 it follows that

$$S_{95}=\frac{r^2}{95\times L_1}-r;\ S_{105}=\frac{r^2}{105\times L_1}-r$$

whence

$$S_{95}-S_{105}=\frac{r^2}{L_1}\left(\frac{1}{95}-\frac{1}{105}\right)$$

The relation

$$S_{95}-S_{105}={}_{95}A_{96}+{}_{96}A_{97}+\text{--------}+{}_{104}A_{105}$$

provides a ready means of checking the arithmetical work and of determining whether the values of the "A" sections have been computed to a sufficient number of places.

The successive "A" sections differ from each other by only about 2 percent, and the fact that they are of moderately low and nearly equal resistance may be a material advantage in reducing the cost of construction. This and the fact that L/r is nearly the same for every position of the switch are the principal advantages of the modified element over the original Waidner-Wolff element.

H. L. Curtis, of this Bureau, has designed and had constructed a number of elements which are intermediate between the element just described and the Waidner-Wolff element.

In bridges which are balanced by making small changes in one of the ratio arms, the entire resistance of the variable ratio arm may be made up of one or more elements of the kind described. In such cases it is convenient to make the resistance of each element or the sum of the resistances of all the elements an "even" value such as 50 or 100 ohms, when all dials are on their mid-setting, in order that the range of the possible change may extend an equal amount above and below the even value. The element described above has an even value of 50 ohms for the mid-setting of the dial, which corresponds to S_{100}. However, it is not convenient to mark this setting 100. Furthermore it should not be marked 0, as this would require the recording of positive and negative readings. A convenient marking is 5, with the markings extending from 0 to X, and the step value marked on the instrument.

If two or more elements are connected in series, it is permissible, if the range of adjustment is small enough, to use a common r for the two lower elements, as shown in figure 2. In principle the values of "A" sections of the 0.001-percent element should be different for each setting of the 0.01-percent element, and conversely. However the "A" sections of the 0.001-percent element are calculated for the mid-setting of the 0.01-percent element and vice versa. As constructed all "A" sections of the 0.001-percent element have the mean of the calculated values. Errors which may result from the effect of the setting of one element on the magnitude of the steps of the other at extreme settings amount to 0.1 step of the lower element.

Figure 2 is a circuit diagram of a resistance ratio set, in which the ratio is adjustable from about 0.994 45 to about 1.005 55 (or 9.9445 to 10.0555) in steps of 0.001 percent. It is used in the testing of bridges and similar apparatus, and the procedure followed is such that the accuracy of the measurements depends not on ratios but on differences of ratios. Consequently the accuracy of adjustment of the principal resistance sections of the ratio set have only second-order effects on the accuracy of the measurements. Usually in a series of measurements the range in ratios is from not less than 0.998 to not more than 1.002 and then, in case the temperature is fairly constant, the quality of the apparatus is such as to justify interpolations to 0.2 step of the lowest element. Except under unusual conditions, differences of readings are reliable to one step of the lowest element, that is, differences in ratios as read from the apparatus are reliable to 1 part in 100 000 of the ratio corresponding to mid-settings of all dial switches. The original apparatus has been used in practically every test of a Wheatstone bridge, Thomson bridge, precision rheostat, and similar apparatus made in the electrical resistance laboratory during the past more than 20 years.

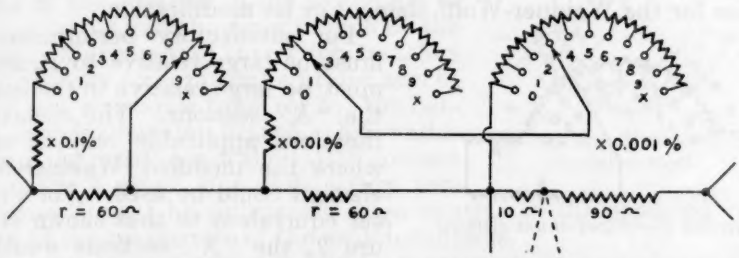

FIGURE 2.—*Bridge ratio arms adjustable in steps of 0.1, 0.01, and 0.001 percent, by means of three modified Waidner-Wolff elements*

Dial-switch positions are numbered from 0 to X, though the ratio is nominally either 1 or 10 when the reading is 555×0.001-percent.

A modification of this ratio set having one more element and giving considerably higher precision was constructed in this Bureau more than 15 years ago and since then has been in regular use in the comparison of precision resistors (resistance standards). The principal resistance sections are of the double-walled sealed type containing no oil, though all resistance sections are kept in a thermostated oil bath. The switches are of good quality and operate under oil. The resistance of one section is adjustable from about 49.5555 to about 50.6665 ohms in steps of 0.1, 0.01, 0.001, and 0.0001 ohm. In use this section is connected in parallel or in series with a 50-ohm section (or occasionally in series with a 50- and 900-ohm section), making an adjustable bridge arm having a nominal value of 25 or 100 ohms (or 1 000 ohms).

With the nominal value either 25 or 100 ohms, steps of the lowest element correspond to parts per million of the nominal value. With the nominal value 25 ohms the current through switch contacts is approximately $\frac{1}{22}$ of the current through the bridge arm. Consequently the effect of variations of the resistance of dial switch contacts is approximately $\frac{1}{484}$ of what it would be with switch contacts directly in series. When the nominal value is 100 ohms the effect of variations

of the resistances of dial switch contacts, expressed in proportional parts, is the same as when it is 25 ohms.

The apparatus was intended to give directly differences of resistance ratios to a precision of 1 part per million when the ratios are within the mid-tenth of its range of adjustment which is 1.111 percent. However it has recently been used in comparing resistance standards to a precision of about 1 part in 10 million, but not without the application of calibration corrections in cases in which the range in adjustment used has been in excess of 0.05 percent.

To a limited extent both of the circuits described above are being used elsewhere.

IV. THE FIXED-SHUNT ELEMENT

Instead of changing the resistance of the shunt, as in the elements so far described, the brush contact might be made to points between sections of the smaller resistance, leaving the shunt of fixed resistance as is shown in figure 3. The resistances for the various sections can be calculated by direct methods, or short-cut methods can be devised if this is desired. The equations will in general be less simple than those for the Waidner-Wolff element or its modification.

FIGURE 3.—*Fixed-shunt element.*

For satisfactory performance S must be large relative to P, and P must be large relative to the sum of the "A" sections. The element is therefore applicable only in cases where the modified Waidner-Wolff element could be used. For a ratio set equivalent to that shown in figure 2, the "A" sections would be fully one order smaller and relatively more nearly equal, which may be advantageous in some cases.

A defect of this arrangement, which may or may not be serious, is that during the time the dial switch is being changed from one setting to the next higher or lower setting, it must make contact with two adjacent contact studs, thus temporarily short-circuiting one section. For the higher elements, if the current through the shunt is one-sixth the total current, the effect of short-circuiting corresponds to about three steps of the dial switch, but here it is of little consequence since in bridge (or in potentiometer) measurements, changes in settings of the dial switches of the higher elements are not made except when the battery (or galvanometer) branch is open. For the lowest element the effect would be considerably reduced by the normal resistance of connectors from junctions between "A" sections and the brush contact surfaces. For the lower elements the effect might easily be reduced to such an extent that it would be scarcely noticeable, by the addition of small resistances in the connections between "A" section junctions and switch contact surfaces, especially if a fairly quick-acting dial switch were used. While this arrangement has not been used it will probably be tried should occasion arise for constructing another adjustable ratio set for a bridge or similar apparatus.

V. THE MOVABLE-BRANCH-POINT ELEMENT

A distinction, which is of some importance in the subsequent discussion, is made here between a terminal which is inherent in the element, and a lead, any number of which may be attached to any one terminal. The elements so far described may be characterized as two-terminal elements, for while the separate resistors in general have four terminals, the complete element has only two terminals. In all figures, terminals of elements or groups of elements are represented by solid circles.

The simplest of the elements having more than two terminals is the movable-branch-point element which has three terminals and is somewhat similar to the Thomson-Jenkin slide described by Varley in 1866 and to the elements used in the White two-battery potentiometer. It is shown in figure 4 in which Z represents a bridge arm of fairly high resistance. The "A" sections to the right (or left) of the position of the dial switch are in a bridge arm of relatively low resistance adjacent to the Z arm. The "A" sections to the left (or right) of the position of the switch are in the battery or galvanometer branch of the bridge. Movement of the switch transfers "A" sections to (or from) a bridge arm of fairly low resistance from (or to) the battery or galvanometer branch, while variations of the resistance of the switch contact are in the Z arm. For satisfactory performance Z must be sufficiently large relative to the expected variations of the resistances of the switch contacts.

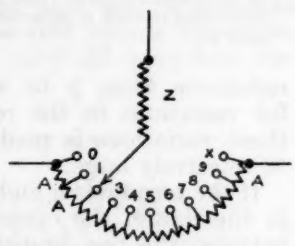

FIGURE 4.—*Movable-branch-point element.*

In resistance-thermometer bridges constructed in accordance with designs developed in this Bureau, the Z arm is one of two equal ratio arms, and the current through the ratio arms is equal to that through the other arms. In typical cases the resistance of each ratio arm is about 20 times that of the adjacent low-resistance arm, consequently the effect of variations of the switch contacts or of thermoelectromotive forces in the switch is about 1/20 as large as though the switch were in either of the low-resistance arms. These advantages are secured with no sacrifice of performance in other respects. The element was also used independently in a commercial type of Thomson bridge of American make, before it was used in resistance-thermometer bridges.

VI. THE PARALLEL ELEMENT

In some resistance-measuring apparatus it is necessary to keep the sum of the resistances of the two bridge arms constant as well as to keep the effect of variations of the resistances of dial switch contacts small. In potentiometers it is necessary to keep the resistance of the battery circuit constant and in some cases to minimize the effect of variations of the resistance of switch contacts and thermoelectromotive forces in the dial-switch contacts. Consequently, if Waidner-Wolff elements are used, they must be in duplicate, that is, two similar elements must be mechanically connected in such manner that as the resistance of one is increased the resistance of the other is decreased by the same amount and these two serve as a single element.

White appears to have been the first to do this. A simpler and better arrangement is the four-terminal element shown in figure 5. All "A" sections, of which there may be any even number, are of equal resistance. The dial switch is of the double-contact type and usually the section M is mounted to rotate with the switch. In figure 5, p,q,w, and v represent the four terminals inherent in the element and a,b,c, and d represent four connected leads. If a and d are used as current leads and b and c are used as potential leads, the notation R_{abcd}, denotes the four-terminal resistance defined by the drop in potential from b to c divided by the current entering on a and leaving on d. This resistance is equal to nA and is adjustable in steps of A. The resistance from p to w equals $10A+M$, and is constant, except for variations in the resistance of switch contacts. The effect of these variations is made relatively small by making the resistance M relatively large.

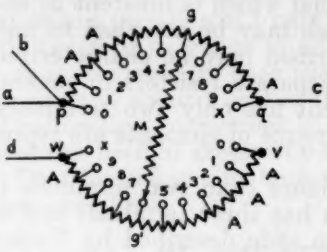

FIGURE 5.—*Parallel element; shown with two leads connected to terminal* p, *and one lead connected to each of terminals* q *and* w.

If the terminals q and v are connected by a resistance t, not shown in the figure, the current entering on a and leaving on d divides between the two branches gMg′ and gqtvg′ inversely as the resistances of these branches. If the current through M is the fractional part f, of the total current, the four-terminal resistance R_{abcd} is adjustable in steps of fA.

VII. COMBINATIONS OF ELEMENTS

A special feature of the parallel element is the manner in which it may be used in combination with other elements of the same or different types. Figure 6 shows one of the parallel elements (marked II) connected in series with a Hausrath six-terminal element (marked I) and in parallel with a Diesselhorst n-step element (marked III). Each of these three types of elements has a double-contact switch, has "A" sections of equal resistances, and the number of "A" sections is twice the number of resistance steps. Element I has six terminals, element II has four terminals, and element III has three terminals. In figure 6, as in figure 5, a and d are current leads, and b and c are potential leads. If the resistances of the "A" sections of element I are 1 ohm, of element II are 0.1333 ohm, and of element III are 0.04 ohm, and if the resistances M and N are so chosen that 0.75 of the current passes through M, and 0.25 through N, the four-terminal resistance R_{abcd} will be adjustable in steps of 0.1, 0.01, and 0.001 ohm, while the resistance between p and w is constant. If the arrangement is to be used as a potentiometer, it is seen that the potential drop from any point to the left of the zero contact block of element II to any point to the right of the X contact block of this element, regardless of what may be to the left or the right, will be changed by this element in steps equal to the resistance of its "A" sections times the current through its dial switch.

If M is 100 ohms, then, with the most unfavorable setting of the dial switches, the resistance of the four-terminal conductor will be affected by a variation of 0.001 ohm in the resistance of the switch contacts of element II to the extent of only 4 microhms. Furthermore, an electromotive force of 10 microvolts in the dial switch affects the potential drop from b to c by only 0.04 microvolt. It should be pointed out that the effects of variations of the resistance of dial-switch contacts, and thermoelectromotive forces in dial switches depend upon the circuit arrangement in which the parallel element (and other elements having more than two terminals) is used. The conclusions stated above concerning the effects of variations of the resistance of dial switch contacts and of thermoelectromotive forces, involve the assumption that neither has an appreciable effect on the current entering on lead a and leaving on lead d.

Figure 7 shows two of the parallel elements (elements II and III) connected in parallel with each other, in parallel with a modified Thomson-Varley slide (element I) and in parallel with a Thomson-Jenkin slide (element IV). Elements I, II, and III have four ter-

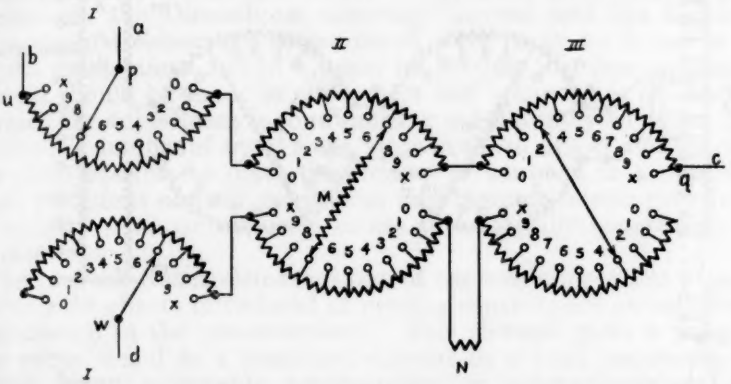

FIGURE 6.—*Parallel element connected in series with a Hausrath six-terminal element and in parallel with a Diesselhorst n-step element; shown with four connected leads* a, b, c, *and* d.

minals each, while element IV has three terminals. This arrangement constitutes two adjustable four-terminal resistances, the sum of which is constant. One of these is the ratio of the potential drop from b to h to the current entering on a and leaving on d, while the other is the ratio of the potential drop from h to f to the current entering on a and leaving on d. The former will be designated R_{abhd} and the latter R_{ahfd}. Obviously moving the double-contact switch of element I downward one step increases R_{abhd} and decreases R_{ahfd} by the resistance of one of the "A" sections of this element. By a proper choice of the resistances of "A" and "M" sections of elements II and III, the sections of element IV, and the "m" sections between elements III and IV relative to the "A" sections of element I, a step of element II may be made 0.1; of element III, 0.01; and of element IV, 0.001 that of a step of element I. Furthermore, the effect of variations of the switch-contact resistances may be made very much less than would be the case if switches of corresponding quality were placed directly in the circuit, that is, if all instead of a relatively

small part of the current passed through switch contacts when p and w are used as current terminals.

A well-known property of four-terminal resistances is that, if both current and potential leads are interchanged, the resistance is not changed. It follows therefore that the effect of variations of the resistances of the dial-switch contacts would be the same if p and v or v and w, instead of p and w, were used as current terminals, even though then all or a large, instead of a relatively small part of the current would pass through some of the switch contacts.

It should be noted that with the arrangement shown in figure 7, the range over which the four-terminal resistors may be adjusted is slightly in excess of the number minus 2, of the "A" sections of element I, times the resistance of the "A" sections of this element. If, for example, element I has 22 sections of 10 ohms each, the four-terminal resistances will be adjustable over a range of slightly more

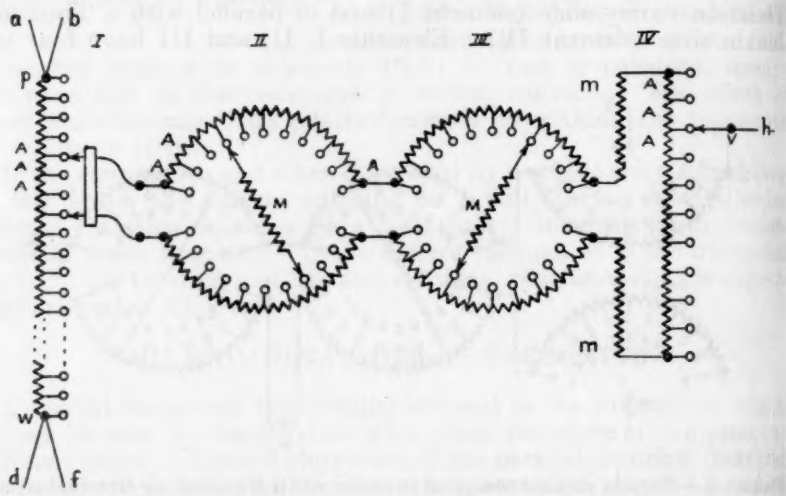

FIGURE 7.—*Two parallel elements connected in parallel with each other, in parallel with a Thomson-Varley slide, and in parallel with a Thomson-Jenkin slide, shown with two equal resistances* m *and* m, *in series with the latter, and with five connecting leads* a, b, h, d, *and* f.

than 200 ohms in steps of 10, 1, 0.1, and 0.01 ohms, while their sum will be slightly less than 220 ohms. It should be pointed out that as the dial switches of the parallel elements are changed in position, they temporarily short-circuit two "A" sections, thus temporarily lowering both of the four-terminal resistances. In cases in which this might be troublesome, the design should be such that, with p and w used as current terminals, the current through the "M" sections is large relative to that through all elements to the right (as shown in figs. 6 and 7) of the element under consideration. Failure to consider the effect of short-circuiting of "A" sections is a mistake made in the design of the first apparatus in which parallel elements were used.

Neither figure 6 nor figure 7 is intended to represent a circuit diagram for an apparatus but merely to show how a parallel element

may be used in combination with other elements of the same or different types. While any number of parallel elements might be used, it is not expected that any case will arise in which it would be advisable to use this type of element exclusively.

VIII. ELEMENTS DEVELOPED ELSEWHERE

Consideration has been given to most of the elements devised and all the elements used in designs developed in this Bureau. Furthermore, the figures show the Hausrath six-terminal element, the Diesselhorst *n*-step element, the Thomson-Jenkin slide, and the Thomson-Varley slide. It should be pointed out that the Hausrath six-terminal element, shown in figure 6, was first described as two slide wires which served both to divide a potentiometer circuit into two parallel branches and as the lowest element of the circuit. Diesselhorst substituted a series of coils of equal resistance for each of the slide wires and, with this modification, it serves best as the highest element of a "split-circuit" potentiometer. Other elements having characteristics more or less similar to those of the Waidner-Wolff element are the Diesselhorst nine-step element and the Hausrath three-terminal element, descriptions of which may be found in the original publications and in a paper by Brooks. In this connection, mention should be made of slide wires and other types of elements in which the adjustment is continuous or substantially so rather than in a limited number of equal steps, since in the design of an apparatus it is often possible to place the contact or contacts in a branch in which variations of their resistances and thermoelectromotive forces are of little or no consequence, or are automatically compensated in the measurements.

The Lindeck-Rothe element is one of the more important of those in which the effects introduced at moving contacts are automatically compensated in the measurements. This element gives a potential drop proportional to a measured current in a fixed resistance, the current being adjustable continuously or substantially so, and measured by a milliammeter or similar deflection instrument which constitutes part of the element. By suitable design, errors which otherwise would result from thermoelectromotive forces and contact resistances may be eliminated to an extent hardly possible in most other types of elements, and for this reason the element is being used by Brooks in a number of designs intended to meet very exacting requirements. A number of arrangements in which measurements depend upon the reading of a deflection instrument have been devised, some of which may be considered modifications of the Lindeck-Rothe element.

Of the elements which have been used for many years, mention should be made of the element devised by O. Wolff and said to have been used previously by Weston, which may be described as two Thomson-Jenkin slide elements mechanically connected in such a manner that as the resistance of one is increased the resistance of the other is decreased by a like amount. While in this element the effects of variations of switch contact resistances and thermoelectromotive forces are not minimized as in most other elements to which reference has been made, it has the advantage that the resistance steps may be larger than in some of the others, and this in some cases may be an

advantage. It is used for the 10, 1, and 0.1 ohm steps of the Wolff-Feussner potentiometer and could be used equally well for larger steps.

Recently both Stein, of the Leeds and Northrup Co., and Bonn, of the Rubicon Co., have proposed elements having characteristics somewhat similar to those of several of the elements considered above, but no description of either has been published.

IX. LIST OF ADJUSTABLE RESISTANCE ELEMENTS

The adjustable resistance elements described above, and others serving more or less the same purpose, to which reference has been made, are listed below. Numbers in brackets in the list below and in the bibliography each refer to items in the other.

1. Thomson-Jenkin slide. [13, 10, 6, 16, 17]
2. Thomson-Varley slide. [13, 10, 6, 16]
3. Waidner-Wolff element. [14, 16, 7, 17, 12, 2]
4. Modified Waidner-Wolff element.
5. Fixed-shunt element.
6. Movable-branch-point element. [12]
7. White movable-branch-point element. [17, 2]
8. Parallel element. [15, 5, 17, 1, 2]
9. Hausrath six-terminal element. [9, 10, 6, 7, 16, 17, 1]
10. Diesselhorst *n*-step element. [6, 7]
11. Hausrath three-terminal element. [9, 6, 2]
12. Diesselhorst nine-step element. [6, 10, 2]
13. Slide wires and other continuously adjustable elements. [8]
14. Wolff element. [18]
15. Lindeck-Rothe element. [11, 6, 3, 4, 2]
16. Stein element.
17. Bonn element.

Considering only those elements which provide both a means of adjusting a resistance and of reading the value to which it has been adjusted, this list should serve to give a good idea of the elements from which, in the design of an apparatus, a selection may be made.

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STANDARDIZATION OF PERMANGANATE SOLUTIONS WITH SODIUM OXALATE

By Robert M. Fowler and Harry A. Bright

ABSTRACT

The titer of permanganate solutions standardized with sodium oxalate by the procedure usually employed (McBride's) has been found to be too high when compared with the values obtained with other primary standards, the error in some cases being as much as 0.4 percent. However, by modifying this procedure the titer obtained with oxalate agrees satisfactorily with the values found with potassium dichromate, pure iron, and arsenious oxide. In the recommended procedure, 90 to 95 percent of the permanganate is added rapidly to a diluted sulphuric acid (5+95) solution of sodium oxalate at 25 to 30° C, the solution warmed to 55 to 60° C and titration completed as usual. Data are presented which show the effect on the new procedure of variations in acidity, temperature, and other conditions.

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I. INTRODUCTION

The procedure generally used in the standardization of permanganate solutions (0.1*N*) with sodium oxalate is that described by R. S. McBride.[1] In this method sodium oxalate is dissolved in 250 ml of diluted sulphuric acid (2+98)[2] and titrated at an initial temperature of 80 to 90° C and a final temperature of not less than 60° C. Further, it is specified that (1) the solution must be stirred vigorously and continuously, (2) the permanganate must not be added more rapidly than 10 to 15 ml per minute, and (3) the last 1 ml must be added dropwise, allowing each drop to become completely decolorized before the next is added. McBride did not cite any data as to the accuracy of this procedure based on comparisons with other primary standards, but concluded from other considerations that the error in the recommended method should not exceed 0.1 percent.

[1] J. Am. Chem. Soc. **34**, 393 (1912).

[2] Throughout this paper diluted acids will be designated as in the following example, "diluted sulphuric acid (2+98)" will mean 2 volumes of the concentrated acid of specific gravity 1.84 diluted with 98 volumes of water.

In his study of the effect of temperature, acidity, rate of addition of permanganate, and other variables, McBride found, as has also been the experience of others, that the titer varies according to the method employed. Consequently, the titration procedure necessary for obtaining an accurate titer must be determined empirically by comparison with other suitable standards.

I. M. Kolthoff [3] has also critically examined the permanganate titration. He recommends a procedure [4] much like that of McBride but makes no specific statement in regard to the rate of addition of permanganate, except to say that it must be added slowly in the beginning. He states that titers so obtained agree within 0.05 percent with those found by means of other primary standards.[5] As will be shown later in this paper, the titer is affected by the rate of addition of permanganate, especially when the titration is made in a hot solution. The excellent agreement claimed by Kolthoff may be due in part to rapid titration, since he states [6] that 100 ml of permanganate was added in three to four minutes. We have found that the titer obtained by Kolthoff's procedure when permanganate (approximately 0.1*N*) is added at a rate of 10 to 15 ml per minute is about the same as that found by McBride's method.

Within the past decade data have accumulated which indicate that the titer of a permanganate solution obtained by McBride's method is from 0.1 to 0.4 percent higher than that found with potassium dichromate through ferrous sulphate.[7] Objections have sometimes been raised in regard to the suitability of potassium dichromate as a primary standard, but recently H. H. Willard and P. Young [8] have shown that the carefully prepared salt is an excellent standard.

Recently, in the analysis of an iron ore (National Bureau of Standards Standard Sample No. 27b), the iron values obtained by titration with a solution of permanganate standardized by McBride's procedure averaged about 0.2 percent higher than those found with solutions prepared from recrystallized and fused potassium dichromate.

This situation led us to make a critical comparison of the titer obtained by McBride's method with that secured by means of other primary standards. As shown in table 1, it was found that the titer given by McBride's method ranged from about 0.2 to 0.45 percent higher than that obtained with potassium dichromate, with pure iron, and with arsenious oxide. In these tests it was observed that small deviations from McBride's directions changed the titer obtained by his method. Such deviations, often made unintentionally, no doubt account for the fact that some analysts apparently have obtained accurate titers by McBride's method.

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[3] Z. anal. Chem. **64**, 185 (1924).
[4] I. M. Kolthoff and N. H. Furman, Volumetric Analysis, **2**, 285 (J. Wiley and Sons, 1929).
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[8] Ind. Eng. Chem., Anal. Ed. 7, 57 (1935).

TABLE 1.—*Comparison of results obtained by standardizing permanganate solutions according to McBride, and by the use of certain primary standards*

$KMnO_4$ solution	Oxalate by McBride's procedure			Recrystallized $K_2Cr_2O_7$ through $FeSO_4$			Pure iron			Arsenious oxide		
No.	Normality	No. of determinations	A. D.[1]	Normality	No. of determinations	A. D.[1]	Normality	No. of determinations	A. D.[1]	Normality	No. of determinations	A. D.[1]
			%			%			%			%
1	0.11066	3	0.03	0.11045	4	0.04	0.11042	2	0.03			
2	.11009	5	.04	.10956	5	.01						
3	.10114	5	.04				.10066	2	.01			
4	.10555	4	.06				.10621	1				
7	.09845	2	.03							0.09811	5	0.02

[1] A. D.=Average deviation from the mean.

The errors in question are outside the limits of accuracy as determined by the end-point corrections and by uncertainties in the atomic weights. While not significant in most commercial work, they are of moment in intercomparisons of primary standards and in certain volumetric analyses such as the determination of iron in materials like high-grade iron ores.

II. DISCUSSION OF THE PERMANGANATE-OXALATE REACTION

The kinetics of the permanganate-oxalate reaction has been studied by a number of investigators, in particular more recently by H. F. Launer and D. M. Yost.[9] It has been shown that the reaction is quite complex and proceeds in several steps, involving compounds containing manganese with valencies intermediate between seven and two, before the end products, carbon dioxide and water are obtained. Atmospheric oxygen also takes part in the reactions.

The concentrations, acidities, etc., employed in these kinetic studies have in general been different from those customarily used by the analytical chemist; consequently he cannot predict from these data but must determine directly the effect of any changed condition on the permanganate-oxalate titer.

McBride determined the effect on the titer of several variations in the titration procedure. His data show that higher titers are obtained both by increasing the temperature and by decreasing the acidity. For example, in diluted sulphuric acid (2+98) the titer was about 0.1 percent higher at 85° C than at 30° C. As regards acidity he found that at 85° C the titer was approximately 0.12 percent higher in (2+98) than in (5+95) diluted sulphuric acid. We have confirmed McBride's findings and have observed further that variations in the acidity cause larger differences in the titer at 85° C than at 30° C.

The titer is also affected by the rate of adding the permanganate, more particularly in hot solutions. McBride found (after the initial reduction of 3 to 10 ml of permanganate) that the titer obtained when the titration was completed in 0.5 minute in diluted sulphuric acid (2+98) at 90° C, was about 0.2 percent less than that found in 5

[9] J. Am. Chem. Soc. **56**, 2571 (1934).

minutes under similar conditions.[10] We have found that the titer obtained in diluted sulphuric acid (2+98) at 85° C when the permanganate is added at a rate of 10 ml per minute is consistently higher (approximately 0.10 to 0.15 percent) than that found when the rate of addition is 20 ml per minute. At 30° C, McBride found little variation in titer with the rate of titration in solutions containing either 2 or 5 ml of sulphuric acid (sp gr 1.84) per 100 ml.

K. Schröder,[11] who also studied this titration, recommended that "The greater part of the permanganate be rapidly run into a strongly acidified solution of the oxalate at 50° C and the titration finished more slowly." McBride, however, concluded that the conditions recommended by Schröder led to a "loss of oxygen."

The rate of stirring also influences the titer. We have observed that rapid motor-stirring yields different values in hot solutions than does stirring by hand. The apparent titer rises with an increase in the agitation of the solution. This effect is especially noticeable when the permanganate is added slowly. At a rate of 10 ml per minute we have observed differences of 0.10 percent or more caused by variations in the rate of stirring.[12]

Several investigators have shown that peroxides are formed during the oxidation of oxalic acid by permanganate. Schröder showed that diluted sulphuric acid solutions of oxalate containing manganous-ion react with air to form peroxide. Launer [13] has shown that oxygen is absorbed, peroxides are formed, and carbon dioxide in excess of the theoretical amount is evolved when an excess of oxalic acid reacts at 25° C with manganous, manganic, and fluoride ions in an acid solution in the presence of air. He observed that for each mole of oxygen absorbed two moles of carbon dioxide were produced, a reaction for which he suggests the following equation:

$$O_2+C_2O_4^{=}+2H^+=H_2O_2+2CO_2$$

Kolthoff [14] has shown that the amount of peroxide formed when oxalate is partially titrated with permanganate increases with rise in temperature and with manganous-ion concentration. He found that no peroxide is formed when titrations are made in an atmosphere of nitrogen with all solutions freed from oxygen. Since peroxide reacts with permanganate before a permanent pink end point can be obtained, an amount of permanganate equivalent to the oxalic acid oxidized by air should be consumed, provided none of the peroxide escapes.

Not all the error in the titer can be accounted for by peroxide formation; if the reaction is performed in an atmosphere of nitrogen, with solutions carefully freed from oxygen, there is still a difference found between rapid titration at 30° C and slow titration at 85° C. For example, our data indicate that even in nitrogen rapid titration

[10] We have found that when titration was made in diluted sulphuric acid (2+98) at 85° C at the maximum rate (i. e., by adding rapidly 99.8 percent of the permanganate from a small beaker and then completing the titration), the titer so obtained averaged about 0.2 percent lower than the value secured by titrating at 10 to 15 ml per minute.

[11] Z. öffentl. Chem. **16**, 270 (1910).

[12] There also appears to be a difference in the titer obtained by McBride's method (i. e., slow titration in hot dilute sulphuric acid (2+98)) in erlenmeyer flasks as compared with beakers. We have found that titers so obtained in a 500-ml erlenmeyer flask may range from 0.05 to 0.15 percent lower than those secured in a 400-ml beaker.

[13] J. Am. Chem. Soc. **55**, 865 (1933).

[14] Z. anal. Chem. **64**, 185 (1924).

in diluted sulphuric acid (5+95) at 30° C (our recommended procedure) yielded titers about 0.2 percent lower than those obtained by slow titration in diluted sulphuric acid (2+98) at 85° C (McBride's procedure).

To sum up, titers tend to be high if titration is made at high temperature, in low acidity, and with slow addition of permanganate accompanied by rapid stirring. In this connection it is perhaps well to point out that McBride has shown that (1) no oxalic acid remains at the end of the reaction, (2) the residual oxidant is no more than the amount required to give the end-point color, and (3) no volatilization of oxalic acid occurs during titration at temperatures below 90° C. Further, Kolthoff [15] found that (4) no significant amounts of oxygen or carbon monoxide could be detected when oxalate was titrated slowly in hot dilute sulphuric acid. It would appear therefore that the above-mentioned factors are eliminated as causing high titers.

III. RECOMMENDED PROCEDURE

Consideration of the foregoing data (section II) indicated that rapid titration at lower temperatures should yield lower titers. Experiments were therefore initiated to examine the magnitude of error when the reaction is conducted at room temperature. At 30° C the reaction in diluted sulphuric acid (2+98) is rather slow. However, when most of the permanganate is added rapidly in diluted sulphuric acid (5+95) at 25 to 30° C and the titration then completed at 55 to 60° C, no end-point difficulties are encountered. A procedure based on these conditions was developed and, as shown later (section IV–2), was found to yield titers that agree well with those obtained with other primary standards.

Procedure.—Transfer 0.3 g of sodium oxalate (dried at 105° C) to a 600-ml beaker. Add 250 ml of diluted sulphuric acid (5+95) previously boiled for 10 to 15 minutes and then cooled to 27±3°C. Stir until the oxalate has dissolved. Add 39 to 40 ml [16] of 0.1*N* potassium permanganate at a rate of 25 to 35 ml per minute while stirring slowly. Let stand until the pink color disappears (about 45 seconds).[17] Heat to 55 to 60° C, and complete the titration by adding permanganate until a faint pink color persists for 30 seconds. Add the last 0.5 to 1 ml dropwise with particular care to allow each drop to become decolorized before the next is introduced.

Determine the excess of permanganate required to impart a pink color to the solution. This can be done by matching the color by adding permanganate to the same volume of the boiled and cooled diluted sulphuric acid at 55 to 60° C. This correction usually amounts to 0.03 to 0.05 ml.[18]

In potentiometric titrations the correction is negligible if the end point is approached slowly.

[15] Z. anal. Chem. **64**, 185 (1924).

[16] 0.3 g of sodium oxalate requires 44.73 ml of 0.1*N* $KMnO_4$.

[17] If the pink color should persist because the permanganate is too strong, discard, and begin again, adding a few milliliters less of the $KMnO_4$ solution.

[18] In very accurate work the correction is best obtained iodometrically (W. C. Bray, J. Am. Chem. Soc. **32**, 1204 (1910)) as follows: cool the titrated solution to 25° C, add 0.5 g of KI, 2 ml of starch solution, and titrate the liberated iodine with 0.02*N* thiosulphate. To obtain the ratio of the thiosulphate to the permanganate solution, add 1 ml of the 0.1*N* permanganate to 300 ml of the diluted sulphuric acid (5+95), stir, add 0.5 g of KI, and titrate with thiosulphate solution, adding starch just before the end point is reached.

IV. TESTS OF THE RECOMMENDED PROCEDURE

1. REAGENTS AND SOLUTIONS

Potassium Permanganate.—Potassium permanganate of reagent quality from several commercial sources was used to prepare solutions that were approximately 0.1*N* and contained 0.1 percent of potassium hydroxide. After aging for at least two weeks the solutions were filtered through purified asbestos into a bottle protected from light. As portions were required for use they were withdrawn through a siphon. The air used to displace the permanganate was passed through glass cotton and alkaline permanganate to remove dust and acid fumes.

Sodium Oxalate.—The sodium oxalate used in this investigation was the National Bureau of Standards Standard Sample No. 40c. Its reducing power was calculated from the certificate analysis as 99.95 percent of the theoretical. Samples were always thoroughly dried at 105 to 110° C immediately before use.

Potassium Dichromate.—Potassium dichromate of reagent quality from two commercial sources was recrystallized twice in platinum. The crystals were dried at 105° C and finally fused in a covered container at 400° C in an electric muffle. The granular salt was preserved in a desiccator, and dried for a short time at 105 to 110° C immediately before use. Approximately 0.1*N* solutions were prepared from accurately weighed amounts of the salt and distilled water.

Pure Iron.—Through the courtesy of the Metallurgy Division of this Bureau, we were fortunate in securing for this work iron wire of very high purity prepared by H. E. Cleaves in connection with another project. While no complete chemical analysis has been made of this material, spectrochemical examination showed faint traces of calcium, magnesium, aluminum, and silicon as the only impurities. The gas content was found to be less than 0.005 percent. The purity of this wire is believed to be at least 99.98 percent. The wire was carefully polished with the finest emery cloth to remove any trace of surface oxide and thoroughly wiped with filter paper immediately before use.

Arsenious Oxide.—The arsenious oxide was the National Bureau of Standards Standard Sample No. 83. Its reducing power was taken as 99.98 percent from the certificate issued with this standard.

Ferrous Ammonium Sulphate.—Solutions approximately 0.1*N* in ferrous iron and containing 10 ml of sulphuric acid per liter were made from ferrous ammonium sulphate of reagent quality. They were saturated with and stored under nitrogen or carbon dioxide.

0.01M Osmium Tetroxide.—0.5 g of osmium tetroxide was dissolved in 200 ml of diluted sulphuric acid (3+97).

Blank determinations were made on the distilled water and acids used. Weight burettes were used in all titrations, so the normalities given in the tables are in gram equivalents per gram of solution. All weights were reduced to vacuum for the intercomparisons. Intercomparisons of the permanganate with other standards were always made within the same day to avoid errors caused by any loss of its oxidizing power.

2. COMPARISON OF THE OXALATE TITER WITH THOSE OBTAINED WITH OTHER PRIMARY STANDARDS

The best proof of the accuracy of titers of volumetric solutions is obviously the agreement obtained by means of different primary standards through reactions that are simple, known to be quantitative, and not affected by slight changes in the procedure used for the standardization. The oxidation of ferrous iron with either permanganate or dichromate is a reaction of this character. Therefore, if the titers of permanganate solutions based on sodium oxalate agree with those found with pure iron and with potassium dichromate, then the oxalate titer by the procedure used is very probably accurate within the errors of the comparison.

The standardization of the permanganate by means of the dichromate was made by titrating 50- to 60-g portions of approximately 0.1*N* ferrous ammonium sulphate in a volume of 300 ml of diluted sulphuric acid (5+95) with each of the two oxidizing agents; the theoretical titer of the dichromate was calculated from its weight. The end points were determined potentiometrically.

The following procedure was used in obtaining the titer of the permanganate solution by means of pure iron:

0.3- to 0.35-g portions of the iron were dissolved in approximately 100 ml of diluted sulphuric acid (20+80) which had been boiled and cooled under carbon dioxide. To prevent loss by spraying, the wire was dissolved in a flask fitted with a vertical condensing arrangement to wash all escaping gas. A slow stream of carbon dioxide was passed through the flask during the whole operation. After the wire had dissolved, the solution was cooled to 25° C and about 90 percent of the iron was titrated in the flask in an atmosphere of carbon dioxide. The solution was then transferred to a beaker and the titration finished potentiometrically under carbon dioxide. The final volume was 300 to 400 ml and contained from 5 to 10 ml of sulphuric acid (sp gr 1.84) per 100 ml of solution. The end point was approached by adding 0.01- to 0.02-ml increments of solution, and the maximum change in potential was taken as the end point.

The dichromate and pure iron were also compared by the method described in the preceding paragraph. It will be noted in table 2 that the agreement between these two standards is within the usual experimental error.[19]

TABLE 2.—*Titration of iron with* $K_2Cr_2O_7$

Wt Fe taken	Fe found	Difference	Error	Remarks
g	g	mg	%	
0.3000	0.2999	−0.1	−0.03	Titrated with $K_2Cr_2O_7$ solution prepared from lot 1.
.3509	.3508	−.1	−.03	Do.
.3504	.3505	+.1	+.03	Do.
.3520	.3518	−.2	−.06	Do.
.3322	.3322	----------	----------	Titrated with $K_2Cr_2O_7$ solution prepared from lot 2.
.3342	.3342	----------	----------	Do.

[19] It has been reported that the end point obtained when ferrous iron is titrated potentiometrically with dichromate varies with the concentration of iron and with the acidity. This is true in part, but the effect is significant only when titrations are made in relatively small or large volumes. Our data show that titrations made in a volume of 350 to 400 ml of diluted sulphuric acid (5+95) to (10+90) are independent of amounts of iron between 0.1 and 0.5 g.

The titer through arsenious oxide was obtained by K. Gleu's method,[20] in which osmium tetroxide is employed as a catalyst. The following procedure was used: 0.3 g of arsenious oxide was transferred to a 600-ml beaker and 10 ml of a sodium hydroxide solution (20 g of NaOH to 100 ml of water) was added. When the arsenious oxide had completely dissolved, 200 ml of diluted sulphuric acid (3+97), previously boiled and cooled, and 5 drops of 0.01*M* osmium tetroxide were added. The solution was then titrated with permanganate. The last 5 to 6 ml were added dropwise [21] and the end point determined potentiometrically.

Table 3 shows that the maximum difference between the titer of permanganate solutions based on sodium oxalate and the recommended procedure, and those found with potassium dichromate, pure iron, and arsenious oxide is 0.06 percent. It appears therefore that the recommended procedure leads to a consumption of permanganate very closely in accordance with the equation,

$$2KMnO_4+5H_2C_2O_4+3H_2SO_4=10CO_2+2MnSO_4+K_2SO_4+8H_2O$$

TABLE 3.—*Comparison of results obtained by standardizing permanganate solutions according to the recommended procedure, and by the use of certain primary standards*

$KMnO_4$ solution no.	Oxalate by recommended procedure			Recrystallized $K_2Cr_2O_7$ through $FeSO_4$			Pure iron			Arsenious oxide		
	Normality	No. of determinations	A. D.[1]	Normality	No. of determinations	A. D.[1]	Normality	No. of determinations	A. D.[1]	Normality	No. of determinations	A. D.[1]
			%			%			%			%
5	0.11850	5	0.01				0.11843	2	0.02			
6	.12471	2	.01	0.12472	3	0.03						
7	.09816	7	.02	.09816	4	.02				0.09811	5	0.02
8	.09810	6	.01				.09810	4	.05			
9	.10322	4	.02							.10319	9	.02

[1] A. D.=average deviation from the mean.

3. EFFECT ON THE RECOMMENDED METHOD OF VARIATIONS IN THE DESCRIBED PROCEDURE

Titers obtained by McBride's method have been shown to vary significantly as the rate of adding permanganate, the acidity, and other conditions are changed. Table 4 presents data showing the effects of these variables in the recommended procedure.

[20] Z. anal. Chem. **95**, 305 (1933).

[21] Our tests indicated that an excess of permanganate is consumed if the latter part of the titration is made too rapidly.

TABLE 4.—*Effect of small departures from the recommended procedure*

[Titer obtained by recommended procedure =0.12471*N*]

Temperature (°C)	Normality
15	0.12466
19	.12470
31	.12472
36	.12482
Rate: $KMnO_4$ per minute (ml)	
20	.12472
10	.12482
Total $KMnO_4$ added at start (%)	
50	.12480

It will be noted that the temperature effect is negligible between 20 and 30° C. Above 30°, the titer begins to increase slowly. Further, the rate of addition of the first portion of the permanganate has little effect on the titer, provided 90 to 95 percent of the permanganate required is added at a rate above 20 ml per minute. Decreasing the rate of addition of the initial portion to 10 ml per minute yields a small increase in the titer. An initial addition of only 50 percent of the required permanganate raises the titer slightly, so, as previously mentioned, it is desirable to add 90 to 95 percent of the permanganate at the start of the titration.

The titer is only slightly affected by a moderate increase in acidity above that recommended. For example, titrations in diluted sulphuric acid (10+90) indicated a titer about 0.05 percent lower than that obtained by the recommended procedure.

Any large increase in the manganous-ion concentration tends to raise the apparent titer although small amounts cause only a slight change. An addition of manganese sulphate, equivalent to 10 ml of a 0.1*N* permanganate, added at the start of a titration, caused no significant change in the titer, though it reduced the time required for the initial clearing of the solution by 50 percent.

V. SUMMARY

McBride's method for the standardization of permanganate solutions with sodium oxalate (i. e., slow titration in hot diluted sulphuric acid (2+98)) yields titers that are too high, the error in some cases being as much as 0.4 percent.

A procedure is recommended for the exact standardization of permanganate with sodium oxalate. In this method 90 to 95 percent of the permanganate is added rapidly to a diluted sulphuric acid (5+95) solution of the oxalate at 25 to 30° C, the solution warmed to 55 to 60° C and the titration completed, the last 0.5 to 1 ml portion being added dropwise. The titer so obtained agrees with those found by means of other primary standards within the limits of experimental error.

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HEAT CAPACITY, ENTROPY, AND FREE ENERGY OF RUBBER HYDROCARBON

By Norman Bekkedahl and Harry Matheson

ABSTRACT

Measurements of heat capacity were made on rubber hydrocarbon in its different forms from 14 to 320° K with an adiabatic vacuum-type calorimeter. At 14° K the heat capacity was found to be 0.064 j/g/°C for both the metastable amorphous and the crystalline forms. With increase in temperature, the heat capacity increases gradually up to a transition at about 199° K, the amorphous form having a little the greater value. At 199° K both forms undergo a transition of the second order, the heat capacity rising sharply. For the amorphous form above this transition the heat capacity rises gradually without discontinuity to the highest temperature of the measurements. The crystalline form undergoes fusion (a transition of the first order) at 284° K, the heat of fusion being 16.7 j/g. At 298.1° K the heat capacity of the rubber is 1.880 ± 0.002 j/g/°C. Utilization of the data according to the third law of thermodynamics yields 1.881 ± 0.010 j/g/°C for the entropy of rubber at 298.1° K. Combination of these with appropriate other data on entropies and heats of reaction yields 1.35 ± 0.10 kj/g for the standard free energy of formation at 298.1° K of rubber from carbon (graphite) and gaseous hydrogen.

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I. INTRODUCTION

The best method for obtaining the free energy of formation of rubber is by making use of the third law of thermodynamics. This makes necessary the determination of heat-capacity values of the rubber in the temperature range from that of room down to temperatures sufficiently low to apply an empirical formula for obtaining the values below this lower temperature. From these heat-capacity values the entropy may be obtained. Then from this latter value, along with the entropy values of carbon (graphite) and gaseous hydrogen and the heat of formation of rubber, a reliable value for the free energy of formation of rubber may be calculated.

Several investigators have previously determined the heat capacities of rubber, but their observations were not made at temperatures

sufficiently low to permit accurate extrapolation to the absolute zero in order to apply the third law. Furthermore, in the previous work the possibility that rubber at low temperatures might exist either as a metastable amorphous form or as a crystalline form was not clearly recognized. In the present investigation the aim was not only to extend the temperature range but also to obtain data of a higher order of accuracy than that previously reported.

II. RUBBER SAMPLE INVESTIGATED

The sample of rubber used in this investigation was prepared by the digestion of latex with steam at about 190° C and the subsequent extraction of the resins and the products of hydrolysis with alcohol and water [20].[1] Where the term rubber or rubber hydrocarbon is used without qualification in this paper, the foregoing product is understood. The sample, of mass 38.30 g, was cut into small pieces, roughly 10 mm^3 each, before its introduction into the calorimeter. At that time it gave no indication of any oxidation having taken place. The air surrounding the rubber in the calorimeter container was replaced by helium so there would be no oxidation.

A complete set of values for the heat capacity of the amorphous form of rubber from 14 to 320° K and several values for the crystalline form were obtained within the first several months. During this time the sample container of the calorimeter can remained gastight and no oxidation of the rubber sample could have taken place. However, owing to a forced delay, no further measurements were made with the calorimeter for nearly two years, during which time the calorimeter can developed a leak and the helium was displaced by air. Oxidation of the sample was rapid, and by the time it was removed from the container it had a strong odor of oxidation products and had increased its weight to 39.38 g. The increase in mass was about 2.8 percent, and, if due to oxygen alone, would give an approximate empirical formula $C_5H_8O_{0.1}$ instead of C_5H_8. During the several weeks previous to the removal of the sample from the calorimeter, a complete set of measurements was made on the crystalline form from 14 to 320° K and several measurements were repeated on the amorphous form. The air was pumped from the sample container during these observations, so it was assumed that this final weight of the sample was constant during these later runs. The larger mass was used for the calculations of the results of the latter experiments, while the original mass was used in the calculation of the results of the experiments performed two years before. When calculated in this manner, the heat capacity of the rubber after this oxidation had occurred appeared unchanged, within 0.2 percent, from its value before oxidation, the results on both forms at different temperatures showing no consistent deviation from the earlier values. This seems to indicate that the oxidation had no significant effect on the value of the heat capacity of the rubber as determined in these experiments.[2]

[1] The numbers in brackets here and elsewhere in the text refer to the "References" at the end of this paper.

[2] These results indicate, however, that at room temperature the oxygen taken up by the rubber must have a heat capacity contribution of about 7 cal per oxygen atom if the addition causes no change in the heat capacity per gram of total sample. This value of 7 cal is considerably larger than that usually derived from organic compounds by Kopp's rule.

It was not necessary to remove the sample from the container in order to convert it from one form to another. The procedure for obtaining the crystalline form of rubber was to cool the calorimeter to about −40° C, allow it to warm up slowly over a period of several days to 0° C, and then to hold it at this latter temperature for several more days. Previous work [3] has indicated that this is sufficient time to obtain complete conversion into the crystalline form. Incomplete conversion would liberate heat in the temperature range from −40 to 0° C, which would easily be noticed from the behavior of the calorimeter during the heat-capacity measurements, as was actually found to be the case on several occasions.

III. CALORIMETER AND ITS OPERATION

The calorimeter used for the measurements of the heat capacities and the heat of transition was of the adiabatic and vacuum type described by Southard and Brickwedde [33], which is an improvement on the type originated by Eucken [8]. The object of the vacuum surrounding the sample container is to minimize the exchange of heat between the container and its surroundings as caused by gaseous conduction and convection. The calorimeter was made adiabatic by surrounding the sample container with a shield which, by means of controlled electrical heating, could be kept the same temperature as the sample, thus minimizing heat leakages to and from the sample. The calorimeter is described in detail by Southard and Brickwedde and only a few general statements need be made here. After the introduction of the sample into its container, the remaining air in the container was replaced by helium at about 1 atmosphere pressure before the container was sealed. Air could not be left inside because it would permit oxidation of the rubber and also because it would liquefy at low temperatures. A vacuum in place of the helium would not be as suitable because the lack of thermal conducting qualities would necessitate too long a time for the sample to reach temperature equilibrium, which was found to be the case in the latter experiments.

Measurements of temperature were made by means of a resistance thermometer of platinum containing 10 percent of rhodium, the resistance of which was about 150 ohms at room temperature. From 14 to 90° K its calibration was made against a helium gas thermometer described by Southard and Milner [34]. Above 90° K it was calibrated against a standard platinum resistance thermometer in a precision cryostat designed and built by Scott and Brickwedde [30]. Resistances were measured by means of a Wenner potentiometer [2, 37], potentials being obtained across the thermometer and also across a 100-ohm standard coil in series with the thermometer when a current of about 1 milliampere was passing through the circuit. This current was supplied by a 2-volt lead storage battery. The precision of the temperature measurements was within 0.002° C above 90° K and within 0.01° C at lower temperatures.

This thermometer was also used as a heater. The current and voltage during the heating were also measured with the same potentiometer, using a 1-ohm standard resistance coil and a volt-box with a ratio of 150:1. Lead storage cells of 120 volts were the source of the heating current. The time of heating was regulated by an automatic switch connected to time signals, which gave a measure of time to

within 0.01 second. The time of heating was varied from 5 to 30 minutes, the heating current from 0.03 to 0.1 ampere, and the temperature from 0.5 to about 15° C. The amount of heat added could be measured to within 1 part in 10,000, which is greater precision than is necessary, since the temperature rise could sometimes be measured only to about 1 part in 1,000. It was not found difficult to control the shields so that the sample would remain constant in temperature within 0.002° C for an hour, even when its temperature was many degrees above that of the surrounding external bath. An actual test of the heat exchange to and from the sample was made with an external bath of liquid hydrogen at about 20° K, the sample and its container at about 90° K, with the shields a little more than a degree higher. Here the temperature of the sample rose 0.15° C per hour. With the shields only 0.4° C higher, the rate of temperature rise was 0.04° C per hour. In actual operation of the calorimeter, the temperature of the shields was kept within 0.01° C of that of the sample, and these deviations were not consistent in either direction but tended to balance each other.

Two operators were necessary for conducting experiments with the calorimeter. One made the measurements on the temperature of and the heat energy added to the sample and container, while the other controlled the temperatures of the shields. The latter was done by regulating the current flowing through the heating wires of the shields. After the sample had shown a constant temperature over a period of several minutes, the electrical switch was thrown for the addition of heat. This necessitated a corresponding increase in the quantity of heat to the shields in order to maintain them at the temperature of the sample. The heat to the shields, of course, was not measured. The heat delivered to the sample was determined from current and voltage readings made at definite time intervals. When the heating interval was complete the automatic switch was again thrown, this time to stop the heating current. When temperature equilibrium was again established, which generally took from 5 to 10 minutes, the temperature was again measured, and then another heating period started. During these heating periods resistances of the current leads from the heater to the shield were measured. The assumption was made that half the heat produced in these leads went to the sample and container and the other half to the shields. Corrections for this additional current were found to be about 3 parts in 10,000 at room temperature and less at lower temperatures.

IV. HEAT CAPACITIES

The curves in figures 1 and 2 give the relation between heat capacity and temperature, the solid line indicating the amorphous form of rubber and the broken line the crystalline form. The curve is shown in sections so that a larger scale may be used. Figure 3 gives the same curves on a smaller scale, the only points of observation shown being those in the transition range, which are not indicated in figures 1 and 2 because of the scale used. Table 1 gives the heat-capacity values at 5° intervals obtained from the curve. All quantities of heat in this paper are expressed in international joules. The factor for conversion into cal_{15} is 4.1833 [25].

TABLE 1.—*Heat capacities of the rubber hydrocarbon*

Temperature	Form of the rubber hydrocarbon		Temperature	Form of the rubber hydrocarbon	
	Crystalline	Amorphous		Crystalline	Amorphous
°K	J/g/°C	J/g/°C	°K	J/g/°C	J/g/°C
15	0.073	0.073	175	0.995	1.009
20	.117	.117	180	1.018	1.032
25	.161	.161	185	1.041	1.054
30	.202	.204			
35	.240	.243	190	1.064	1.078
			195	1.086	1.102
40	.276	.282	200	1.200	1.440
45	.310	.317	205	1.397	1.603
50	.343	.352	210	1.474	1.615
55	.374	.387			
60	.405	.418	215	1.506	1.628
			220	1.534	1.641
65	.437	.450	225	1.560	1.655
70	.467	.480	230	1.587	1.668
75	.497	.510	235	1.616	1.682
80	.524	.537			
85	.552	.566	240	1.644	1.696
			245	1.664	1.710
90	.579	.596	250	1.684	1.723
95	.605	.622	255	1.704	1.737
100	.629	.646	260	1.723	1.750
105	.656	.673			
110	.681	.697	265	1.743	1.764
			270	1.763	1.777
115	.707	.723	275	1.783	1.790
120	.733	.748	280	1.804	1.805
125	.757	.772	•284	(a)	(a)
130	.781	.796			
135	.805	.820	285	----------	1.822
			290	----------	1.840
140	.829	.844	295	----------	1.865
145	.853	.868	300	----------	1.890
150	.877	.892	305	----------	1.915
155	.901	.916			
160	.925	.939	310	----------	1.940
			315	----------	1.965
165	.948	.963	320	----------	1.990
170	.972	.986			

•Heat of fusion at 284° K is 16.7 J/g.

With the exception of the range of temperature where the crystals are melting, the heat capacities of the crystalline form of rubber are in general lower than those of the amorphous form. This is to be expected because of less randomness of the positions of the molecules in the crystalline form.

Tables 2 and 3 give the data and results of the calculation of one observation on the heat capacity of the crystalline form of the rubber hydrocarbon. Current reversals were made and the values obtained in the two directions were averaged in order to compensate for any stray currents which may have been present in the system. The mean temperature and the rise in temperature were obtained directly from the data in table 2. In order to obtain the amount of heat added, the values of the current passing through the heater and also the potential across the heater (table 3) were plotted as a function of time, and the values at the half-period of heating (6.5 minutes) were taken as the average. Both the current and the voltage show straight-line relationships with time over short intervals such as this unless the sample is undergoing a transition, in which case there will appear a change of slope of the voltage curve with time.

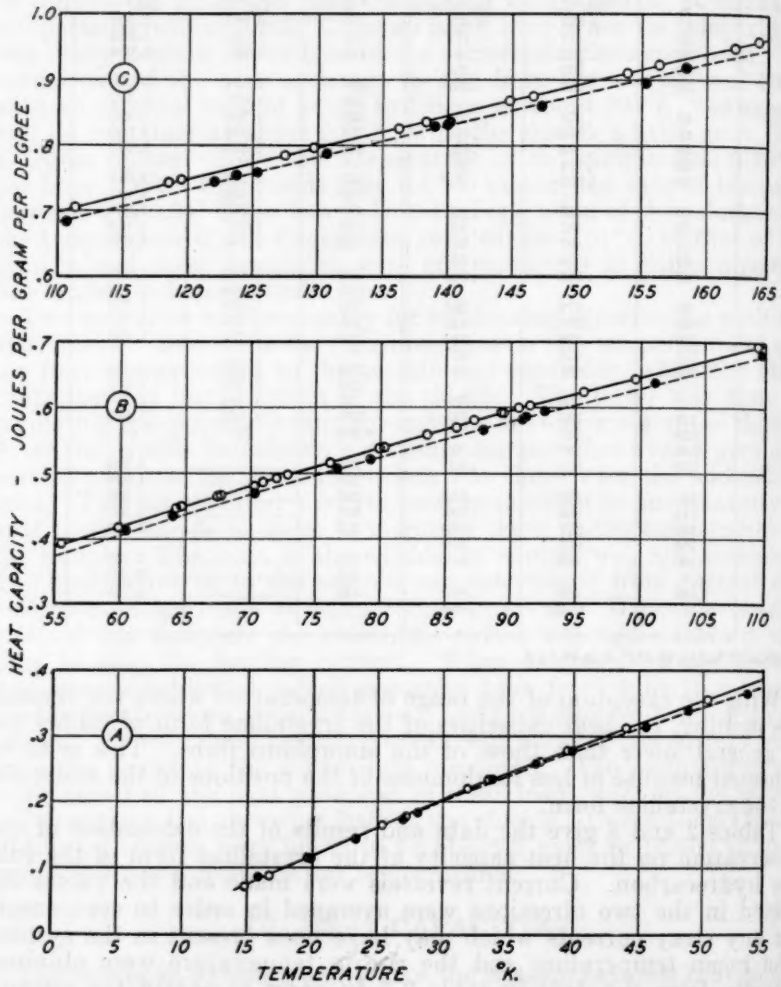

FIGURE 1.—*Relation between heat capacity of rubber hydrocarbon and temperature.*

The dotted line represents the crystalline form and the solid line the amorphous. (See fig. 2 for other half of curve.)

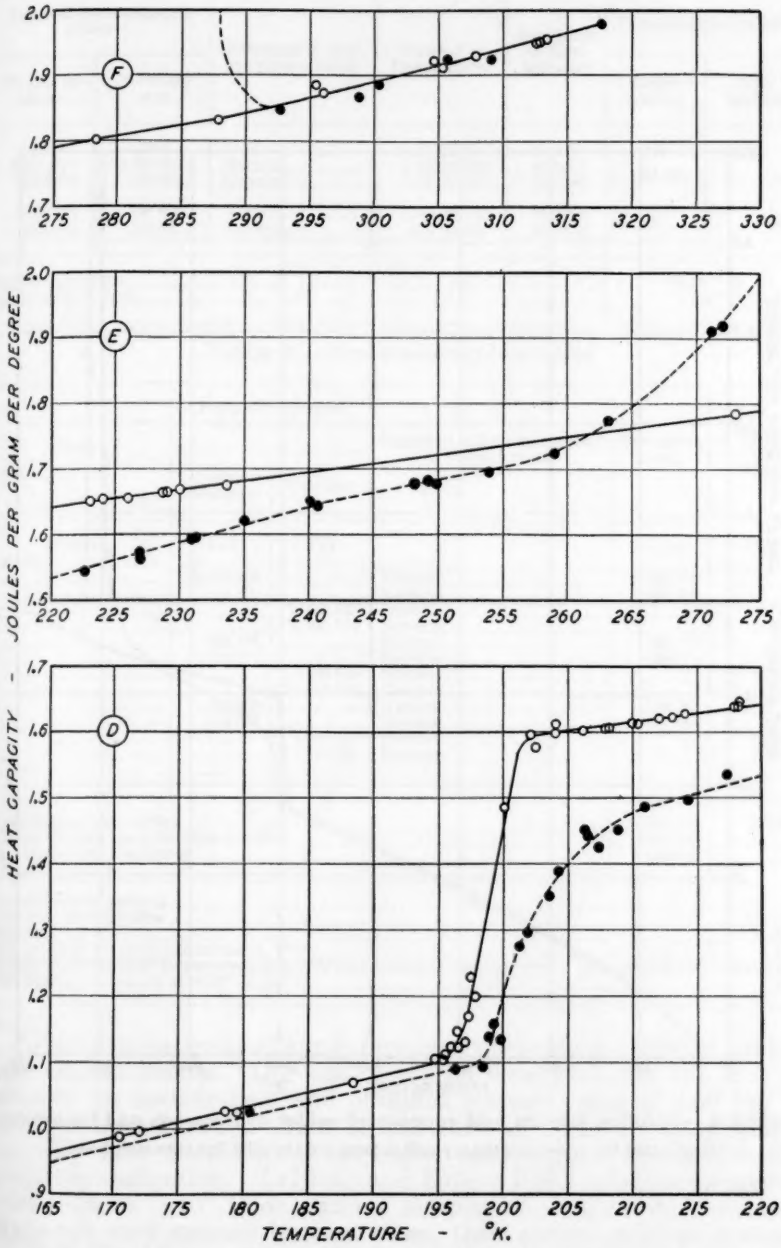

FIGURE 2.—*Relation between heat capacity of rubber hydrocarbon and temperature.*

The dotted line represents the crystalline form and the solid line the amorphous. (See fig. 1 for other half of curve.)

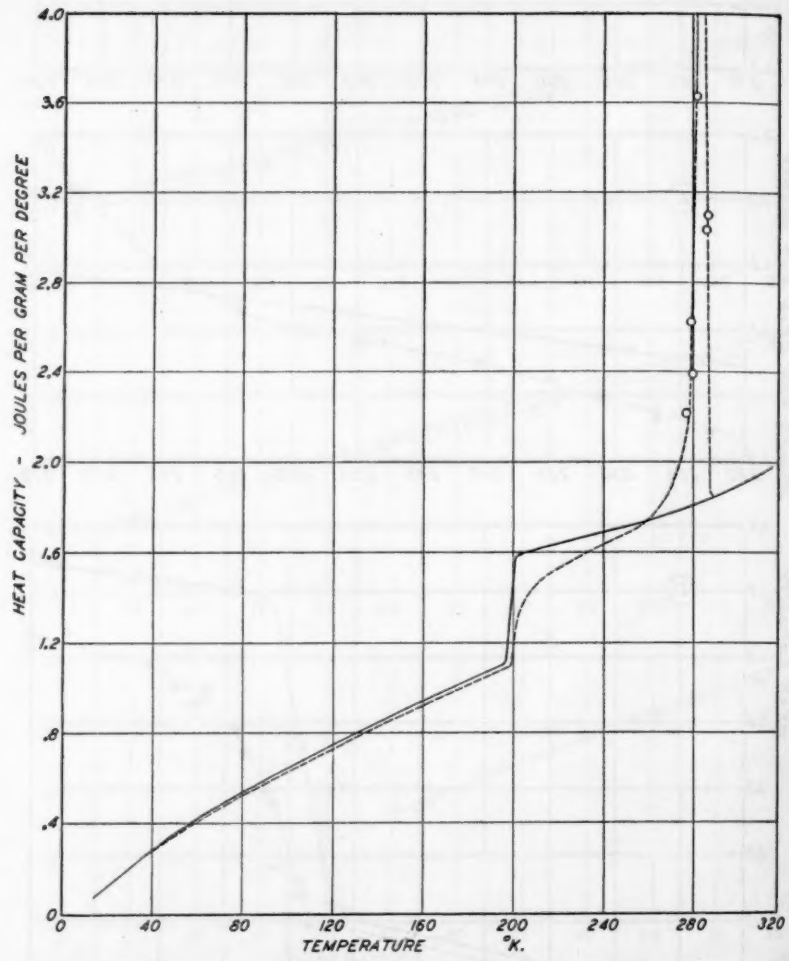

FIGURE 3.—*Relation between heat capacity of rubber hydrocarbon and temperature.*
The dotted line represents the crystalline form and the solid line the amorphous.

TABLE 2.—*Measurements of temperature before and after heating*

Potential measurements across—		Direction of thermometer current	Current in thermometer	Resistance of thermometer	Temperature of sample	
100-ohm resistance	Thermometer				Before heating	After heating
Volt	*Volt*		*Ampere*	*Ohms*	°K	°K
0.099 999 5	0.088 902 0	Normal	0.000 999 995	88.902 4	65.662	
.099 999 0	.088 901 2	Reverse	.000 999 990	88.902 0		
.100 014 5	.091 500 0	Normal	.001 000 145	91.486 7		74.900
.100 014 5	.091 497 5	Reverse	.001 000 145	91.484 3		
Mean temperature					70.281° K	
Rise in temperature					9.238° K	

TABLE 3.—*Measurement of heat added*

Time	Potential measurements across—		Direction of battery current to potentiometer	Current in heater	Potential across heater
	1-ohm resistance	Volt-box			
Minutes	*Volt*	*Volt*		*Ampere*	*Volt*
0 (begin)					
1	0. 058 393		Normal	0. 058 393	
2	. 058 393		Reverse	. 058 393	
3		0. 034 657	Normal		5. 198 9
4		. 034 729	Reverse		5. 209 7
5	. 058 374		Normal	. 058 374	
6	. 058 374		Reverse	. 058 374	
7		. 034 938	Normal		5. 241 0
8		. 035 006	Reverse		5. 251 2
9	. 058 355		Normal	. 058 355	
10	. 058 353		Reverse	. 058 353	
11		. 035 217	Normal		5. 282 9
12		. 035 283	Reverse		5. 292 8
13 (end)					
Mean values (from curve)				. 058 370	5. 235 5
Current through the 3,000-ohm volt-box				. 001 745	
Current through the heater				. 056 625	

Time of heating, seconds	780
Total heat added, joules	230. 46
Heat added, j/°C	24. 95
Heat absorbed by empty calorimeter, j/°C	6. 45
Heat absorbed by 39.38 grams of sample, j/°C	18. 50
Heat capacity of sample at 70.28° K, j/g°C	. 4698

Previous investigators have determined the heat capacities of rubber with various results. Gee and Terry [9] were probably the first to measure the specific heat and obtained a mean value of 2.00 j/g/°C on raw rubber between about 20 and 100° C. This compares fairly favorably with the results at the higher temperatures obtained in the present investigation. LeBlanc and Kröger [19] made measurements from −70 to +40° C on various samples of smoked sheet rubber. While not very smooth in most cases, their curves gave an average value of about 2.2 j/g/°C at 25° C, which is considerably higher than the value 1.88 indicated in figure 2. Ruhemann and Simon [29] obtained a value of about 2.1 j/g/°C for smoked sheet at 25° C. Boström [5] reported an average value of 1.55 j/g/°C at 17° C, which is lower than the 1.85 value obtained in the present investigation. Ruhemann and Simon's value for the specific heat at −80° C was

about 1.2 j/g/°C as compared with 1.09 for that temperature as indicated in figure 2. In an earlier investigation on the heat of vulcanization of rubber [21], mean heat-capacity values were obtained between 25 and 175° C. The average mean value obtained for both crude and purified rubber was 2.17 j/g/°C, which seems quite reasonable from the trend of the curve of the present investigation.

The curve obtained by Ruhemann and Simon for the heat capacities of smoked sheet from −100 to about −20° C, which includes a transition of the second order [3, 7], which they called the α anomaly, is similar to the one obtained in the present investigation. At 0° C they obtained a hump in the curve which they called the β anomaly, but this break in the curve could not be found in the present investigation. Figure 3 shows that at 284° K a transition of the first order takes place in which there is melting of rubber crystals. This transition was named the γ anomaly by Ruhemann and Simon, but was found by them to take place at a temperature several degrees higher.

The transition obtained at 199° K in this investigation is probably the same as that shown in some previous work on the thermal expansion and dielectric constant of rubber [3], and there reported to take place at approximately 200° K. The temperature of fusion obtained in the present investigation also agrees with that obtained from data on the coefficient of thermal expansion.

V. HEAT OF FUSION

At above 255° K the curve for the heat capacity of the crystalline form begins to rise, owing to the premelting of some of the crystals. Although the fusion temperature is 284° K, there is a great tendency for the rubber to premelt with respect to the average temperature of the calorimeter. The higher local temperature near the heating coil produces a small amount of melting which does not reverse itself when temperature equilibrium is established below the fusion temperature, because the rate of transition from the crystalline to the amorphous form is much greater than that in the reverse direction [3]. This, however, will have no appreciable effect on the value obtained for the heat of melting.

With the rubber in the crystalline form a heating was begun at a temperature of 253.73° K, continued through the transition, and ended with an equilibrium temperature of 291.90° K. The heat required to raise the rubber through this temperature range was 102.605 j/g. On the heat capacity-temperature diagram, a smooth curve was drawn from some point on the curve of the crystalline form just below the beginning of the melting of the rubber (about 250° K) to the curve above the temperature of the transition. The energy required to bring the rubber from 253.73 to 291.90° K, assuming no transition, was obtained by measuring the area under this curve between these two temperatures, and was found to be 85.894 j/g. The difference between these two energy values in 16.71 j/g, which is the heat of fusion of the rubber. This value is in agreement with that obtained in a similar manner by Ruhemann and Simon [29] for frozen smoked sheet. Van Rossem and Loticius [35] report a value of 21.1 j/g for latex sheet at 0° C, obtained from the difference between the heats of swelling of frozen and thawed rubber.

VI. ENTROPY

According to the third law of thermodynamics, the entropy of a substance in the liquid state at 298.1° K is given by the equation

$$S^0_{298.1}=\int_0^{T_{mp}} C_p \text{ (crystals)} d\ln T+\frac{\Delta H_{fusion}}{T_{mp}}+\int_{T_{mp}}^{298.1} C_p \text{ (liquid)} d\ln T.$$

Curves were prepared plotting the values of the heat capacities at constant pressure, C_p, of the rubber hydrocarbon both in the crystalline and the amorphous forms as functions of the logarithm of the absolute temperature T. Since C_p values were obtained only as low as 14° K, the graphic integration of these curves could not be made below this point. Here the Debye approximation formula [6] was used. From tables [31] of the heat capacities and Debye functions, $\beta\nu$, the latter was found to be constant with a value of 120 from 14 to 35° K. From tables [31] of the Debye functions and entropies with a $\beta\nu$ value of 120, the entropy change of the rubber from 0 to 14° K, $\int_0^{14} C_p\, d\ln T$, was found to be 0.015 ± 0.001 j/g/°C for both the amorphous and the crystalline forms.

From the graphic integration of the curves the following values were obtained:

$$\int_{14}^{298.1} C_p d\ln T \text{ (amorphous form)}=1.860 \text{ j/g/°C},$$

$$\int_{14}^{284} C_p d\ln T \text{ (crystalline form)}=1.717 \text{ j/g/°C},$$

$$\int_{284}^{298.1} C_p d\ln T \text{ (amorphous form)}=0.090 \text{ j/g/°C}.$$

The entropy of fusion of the crystalline form of rubber at 284° K,

$$\frac{\Delta H_{284}(\text{fusion})}{T}=0.059 \text{ j/g/°C}.$$

Following the curve for the amorphous form, one obtains

$$S_{298.1}-S_0=\int_0^{14} C_p d\ln T+\int_{14}^{298.1} C_p d\ln T=1.875\pm0.004 \text{ j/g/°C}.$$

From the data on the crystalline form one obtains

$$S_{298.1}-S_0=\int_0^{14} C_p d\ln T+\int_{14}^{284} C_p d\ln T+\frac{\Delta H_{284}(\text{fusion})}{T}+\int_{284}^{298.1} C_p d\ln T=1.881\pm0.010 \text{ j/g/°C}.$$

The third law of thermodynamics states that a pure substance in the crystalline state has zero entropy at the absolute zero of temperature. Any other form may not have zero entropy, as has been found by several investigators [11, 16, 17, 23, 24, 32]. The entropy of rubber at 298.1° K is obtained from the last equation by setting the entropy

of the crystalline form equal to zero at 0° K. Then for rubber at 298.1° K, $S_{298.1}=1.881 \pm 0.010$ j/g/°C.[3]

The above data give for the difference between the entropies for the crystalline and amorphous forms at 0° K the value $(1.881 \pm 0.010)-(1.875 \pm 0.004)=0.006 \pm 0.011$ j/g/°C. This indicates, within the accuracy of the present experimental data, that S_0 (amorphous)$-S_0$ (crystalline) is not greater than 0.017 j/g/°C, or 0.28 cal/°C/C_5H_8 unit.

VII. FREE ENERGY OF FORMATION

Various investigators [4, 12, 15, 18, 22, 36] have determined the heat of combustion of rubber, but the results of Jessup and Cummings [15] are probably the most nearly accurate. Their value for steam-purified rubber at 30° C is 45,239 ±90 int. j/g. Using the values of specific heats of 1.89 j/g/°C for rubber at 27.5° C as determined in this investigation, 8.9 cal/mole/°C for CO_2 [13], 7.0 cal/mole/°C for O_2, and 17.5 cal/mole/°C for H_2O [1], the heat of combustion of the rubber hydrocarbon at 298.1° K is calculated to be 45,250±90 int. j/g.

Using the heats of formation at 298.1° K of gaseous CO_2 taken as -94.24 ± 0.10 kcal/mole [28, 27] and of liquid H_2O -68.313 ± 0.010 kcal/mole [26], the heat of formation of the rubber from its elements, $\Delta H_{298.1}$ is -507 ± 100 j/g. Likewise, from the entropies of carbon (graphite) taken as 1.36 ± 0.03 cal/mole/°C [14] and H_2 31.23 ± 0.00 cal/mole/°C [10], the entropy of formation of the rubber hydrocarbon at 298.1° K, $\Delta S_{298.1}$, is -6.215 ± 0.014 j/g/°C. Then, from the thermodynamic formula $\Delta F=\Delta H-T\Delta S$, the thermodynamic potential or free energy of formation of the rubber hydrocarbon at 298.1° K, $\Delta F_{298.1}=(-507 \pm 100)-(298.1)(-6.215 \pm 0.014)=1{,}345 \pm 100$ j/g, or 1.35 ± 0.10 kj/g, or 21.9 ± 1.6 kcal/C_5H_8 unit.

The authors wish to express their appreciation to various members of the Bureau staff: to A. T. McPherson and F. G. Brickwedde, under whose supervision this investigation was made; to the members of the latter's staff of the cryogenic laboratory for constructing and assisting in the calibration of the thermometer, and for furnishing the liquid hydrogen; and to W. L. Holt for assisting in making some of the measurements.

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DETERMINATION OF MAGNETIC HYSTERESIS WITH THE FAHY SIMPLEX PERMEAMETER

By Raymond L. Sanford and Evert G. Bennett

ABSTRACT

An attachment for the Fahy Simplex permeameter is described by which the H-coil can be quickly rotated end for end. By means of this attachment, values of magnetizing force, H, corresponding to points on a hysteresis loop, can be attained with as high precision as could be attained previously only for points on the normal induction curve. By the use of this attachment, smoother curves are obtained in less time than can be done with the original arrangement.

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I. INTRODUCTION

The Fahy Simplex permeameter[1] is a very satisfactory instrument for the determination of normal induction and hysteresis data for ordinary magnetic materials. Its principal advantages are simplicity and convenience of operation and its ability to indicate the average properties of inhomogeneous materials.[2] However, in common with other methods in which values both of magnetic induction B, and of magnetizing force H, are obtained in terms of deflections of a ballistic galvanometer, the apparatus in its original form does not give hysteresis data with as high precision as can be realized in measurements of normal induction. The reason for this is that points on a hysteresis loop are determined by taking the algebraic difference between the value of B or H corresponding to the tip of the loop and the change observed when the magnetizing current is suddenly reduced from the maximum value to some lower value in either the same or opposite direction. The lack of precision is particularly conspicuous in the measurement of H, especially for the part of the loop in the neighborhood of the coercive force H_c. By reference to figure 1 it can be seen that a determination of the value of H_c, for instance, involves taking the difference between the two quantities H_m and (H_m+H_c), each of which is large relative to the value of H_c. It is obvious that even a small experimental error in the observed values of H_m and (H_m+H_c) may lead to a relatively large percentage error in the value of H_c taken as the difference between them.

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The present investigation was undertaken to find out whether or not it would be feasible to determine the values of H for points on a hysteresis loop by direct measurement instead of by taking differences as indicated above. It was found possible to do this by mounting the H-coil so that it can be quickly turned end for end between the H-blocks by rotating it about a vertical axis through its center. In this way values of H for points on a hysteresis loop can be determined with a precision as great as that formerly attainable only for points on the normal induction curve.

II. DESCRIPTION OF THE APPARATUS

The permeameter with the new H-coil in place is shown in figure 2. A brass framework holds the iron end-blocks in proper position and carries the bearings for the vertical shaft through the middle of the H-coil. It was necessary to make the new end-blocks slightly longer than the original ones to provide for clearance between the magnet-

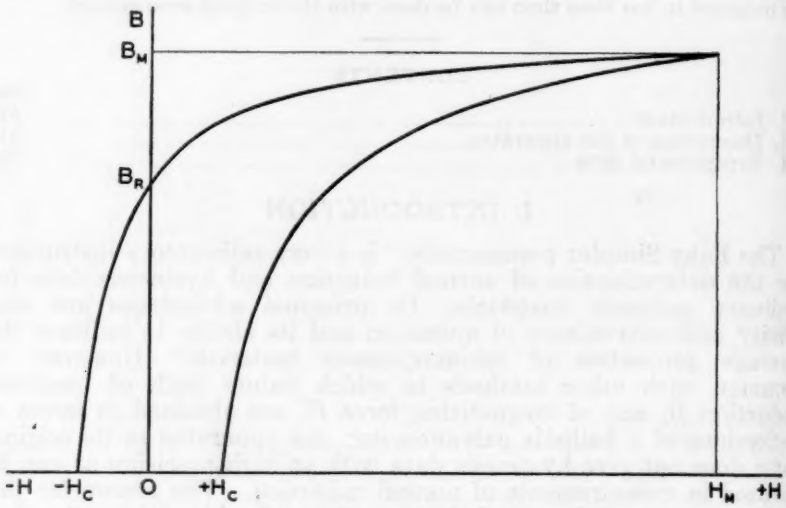

FIGURE 1.—*Upper half of a typical hysteresis loop.*

izing coil and the H-coil when the latter is rotated. A pinion at the upper end of the vertical shaft engages with a rack which also engages with a smaller pinion on the shaft of a small series wound-motor mounted at the back of the permeameter.

Two stops similar to ordinary switch clips limit the rotation of the coil to 180°. These stops receive a brass blade mounted on the H-coil near one end and can be adjusted to regulate the amount of friction. In order to reduce the impact on the apparatus to a minimum, the motor current is cut off before the stroke is completed by means of an automatic switch mounted on top of the apparatus. This switch is actuated by a bakelite block attached to the rack and can be adjusted to cut off the current at any desired point during the stroke. When the switch and stops are properly adjusted, the H-coil can be quickly rotated end for end between the end-blocks without producing an appreciable jar on the apparatus. Connection to the coil is made by means of flexible leads.

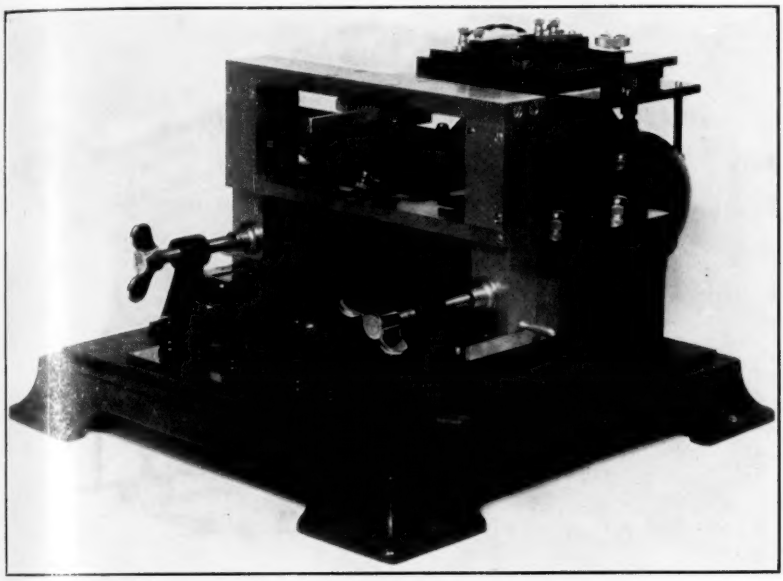

FIGURE 2.—*Permeameter with rotating* H*-coil attached.*

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A diagram of connections is given in figure 3. A source of d-c power is connected at G. The reversing switch F is located at the control table and is operated by the observer. The contacts on the automatic cut-off switch A, are operated by the bakelite block mounted on the rack and are so connected that the armature circuit of the motor is complete only when F is closed in the right direction. When this is done, the motor operates to rotate the H-coil about its vertical axis. At the proper time, the contact at A is opened, thus cutting off the current and allowing the stroke to be completed by momentum. The movement of the block also permits the other contact at A to close so that the coil can be rotated in the opposite direc-

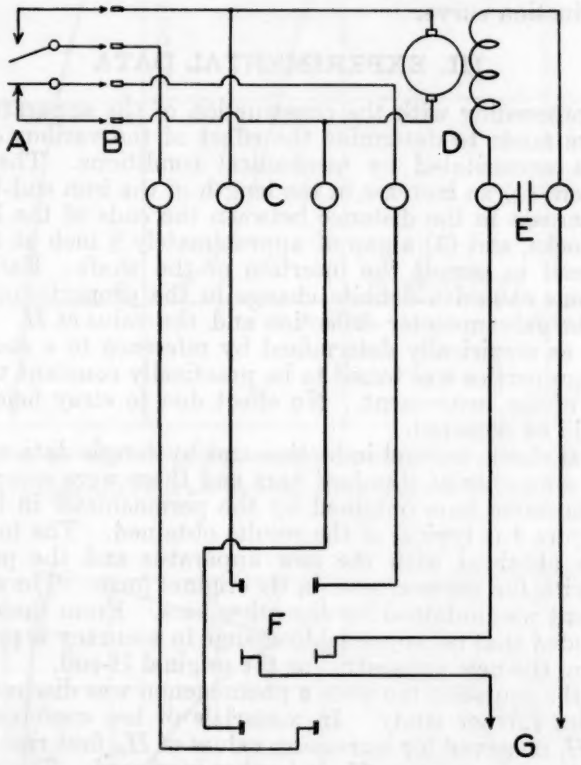

FIGURE 3.—*Diagram of connections.*

tion by reversing switch F. A capacitor E absorbs the inductive surge caused by opening the motor field circuit. B represents a group of plugs and jacks for disconnecting the cut-off switch when the apparatus is to be removed from the permeameter. The apparatus is interchangeable with the regular end-blocks and H-coil.

The cycle of operations to determine a point on a hysteresis loop is as follows. The magnetizing current is set to give the desired H_m and reversed a sufficient number of times to bring the specimen to a cyclic condition. The value of H_m is determined either by reversal of the magnetizing current or by rotating the H-coil. The value of B is obtained by reversal of the current. After the values of B and H

at the tip are established, the current is reduced in the regular way with the galvanometer connected to the B-coil. The value obtained by subtracting the observed change from B_m previously determined is the required value of B. After the current has been reduced to the required value, the galvanometer is connected to the H-coil and the coil is rotated. For this determination, the galvanometer sensitivity is adjusted to a suitable value higher than that used for the determination of H_m. Several check readings can be taken without reestablishing cyclic condition as is necessary when the regular method is used. In this way the value of H corresponding to the desired point on the hysteresis loop can be determined directly, with a precision equal to that obtained in the measurement of a similar value on the normal induction curve.

III. EXPERIMENTAL DATA

Before proceeding with the construction of the apparatus, experiments were made to determine the effect of the various changes in dimensions necessitated by mechanical conditions. The principal changes were (1) an increase in the length of the iron end-blocks, (2) a slight increase in the distance between the ends of the H-coil and the end-blocks, and (3) a gap of approximately ½ inch at the middle of the H-coil to permit the insertion of the shaft. Each of these modifications caused a definite change in the proportionality factor between the galvanometer deflection and the value of H. However, the factor as empirically determined by reference to a standard bar of known properties was found to be practically constant throughout the range of the instrument. No effect due to stray field from the motor could be detected.

As a final check, normal induction and hysteresis data were determined for a number of standard bars and these were compared with data on the same bars obtained by the permeameter in its original form. Figure 4 is typical of the results obtained. The full lines are the curves obtained with the new apparatus and the points were obtained with the permeameter in its original form. The same order of agreement was obtained for the other bars. From these results it was concluded that no appreciable change in accuracy is produced by substituting the new apparatus for the original H-coil.

During the course of the tests a phenomenon was discovered which may require further study. In materials of low coercive force the values of H_c observed for increasing values of H_m first rise to a maximum and then decrease as H_m is further increased. The decrease is observed only for materials having a maximum H_c of the order of 5 oersteds or less. For magnetically harder materials it is not observed. This phenomenon has been noticed before but was attributed to the difficulty in holding H_m sufficiently constant during the observations. With the new method this difficulty is practically eliminated however, so it must be concluded that the error is inherent in the permeameter itself. Figure 5 shows the results for two different materials plotted on a percentage basis. The maximum H_c for curve A is 2.4 oersteds and for curve B is 16.8 oersteds. There appears to be an error of small absolute magnitude in the observed values of H_c which increases with increasing H_m. This error is apparently due to the change in flux distribution in the specimen when the magnetizing

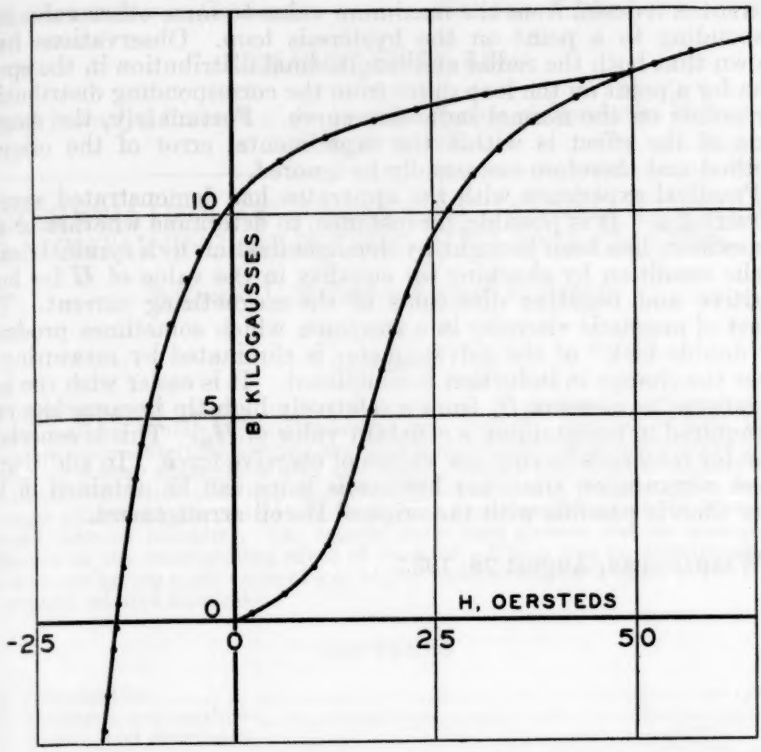

FIGURE 4.—*Agreement between new apparatus and original* H-*coil.*

Curves represent results with new apparatus. Points show results with original H-coil.

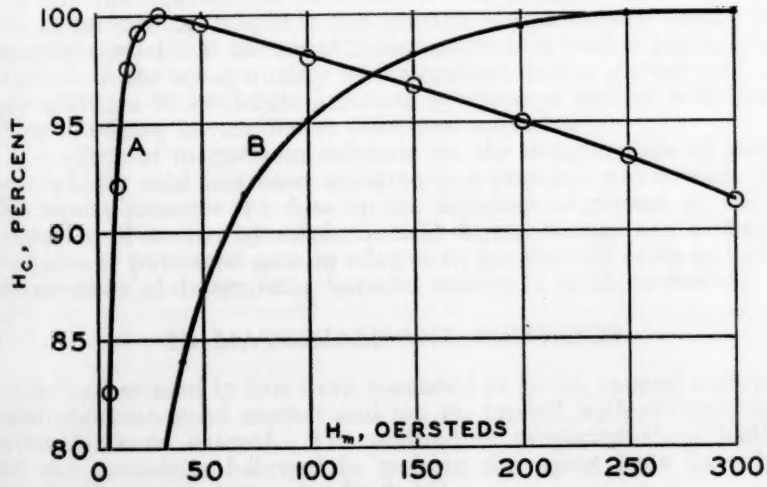

FIGURE 5.—*Observed variation of* H_c *with* H_m *for two different materials.*

Curve A, Max H_c=2.4 oersteds. Curve B, Max H_c=16.8 oersteds.

current is reduced from the maximum value to some other value corresponding to a point on the hysteresis loop. Observations have shown that both the radial and longitudinal distribution in the specimen for a point on the loop differ from the corresponding distribution for points on the normal induction curve. Fortunately, the magnitude of the effect is within the experimental error of the original method and therefore can usually be ignored.

Practical experience with the apparatus has demonstrated several advantages. It is possible, for instance, to determine whether or not a specimen has been brought by demagnetization to a symmetrically cyclic condition by checking for equality in the value of H for both positive and negative directions of the magnetizing current. The effect of magnetic viscosity in a specimen which sometimes produces a "double kick" of the galvanometer is eliminated by measuring H after the change in induction is completed. It is easier with the new apparatus to measure H_c from a relatively high tip because less care is required in maintaining a constant value of H_m. This is especially true for materials having low values of coercive force. In addition to these advantages, smoother hysteresis loops can be obtained in less time than is possible with the original H-coil arrangement.

WASHINGTON, August 28, 1935.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP846

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DETERIORATION OF VEGETABLE-TANNED LEATHERS CONTAINING SULPHURIC ACID AND GLUCOSE

By Everett L. Wallace and Joseph R. Kanagy

ABSTRACT

The influence of glucose on the deterioration of chestnut- and quebracho-tanned leathers containing sulphuric acid was studied. Samples of both kinds of leather, each containing varying amounts of acid, and comparable leathers which contained similar amounts of acid and approximately 5 percent of glucose were examined. Deterioration was measured by determining the change in tensile strength after 0, 12, 18, and 24 months storage under conditions of 70° F and 65-percent relative humidity. The results show that glucose has no measurable influence on the deteriorating effect of the acid. There was no deterioration of the leathers having a pH value of 3 or higher when stored for 2 years at 70° F and 65-percent relative humidity.

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I. INTRODUCTION

In the manufacture of commercial sole leather, filling materials such as magnesium sulphate and glucose are commonly used. It is generally agreed that the use of these materials in leather has no harmful effect on the aging quality of the product during storage and that their addition in moderate amounts produces a leather with better selling qualities, having better color and appearance.

The effect of magnesium sulphate on the deterioration of leather by sulphuric acid has been reported in a previous publication [13].[1] This report presents the data on the influence of glucose on the deterioration of leather by sulphuric acid during storage and is the last of a series of published articles relative to the effect of acids on leather and methods of determining harmful acidity [1 to 15, inclusive].

II. MATERIALS AND METHODS

The leather used in this work consisted of lot 25, tanned with powdered chestnut-wood extract and lot 26, tanned with ordinary solid quebracho-wood extract. The method of preparing these leathers and the procedure followed in making the aging tests have been described in previous reports. [1, 2, 13].

[1] The figures given in brackets in the text correspond to the numbered references at the end of this paper.

The results of the analysis of the leathers before adding the acid and glucose are given in table 1.

TABLE 1.—*The chemical analyses of leather before treatment*

[Results are expressed in percentage of the leather, excepting for degree of tannage and pH]

Items determined	Tannage	
	Chestnut	Quebracho
Water-soluble	7.58	11.55
Hide substance	49.90	44.17
Grease (petroleum-ether extract)	3.23	3.52
Moisture	11.72	10.79
Insoluble ash	0.12	0.07
Combined tannin [1]	27.45	29.90
Total	100.00	100.00
Degree of tannage [2]	55.	68.
Soluble tannins	5.54	9.93
Soluble nontannins	2.04	1.62
Total ash	0.24	0.12
pH [3] (glass electrode)	3.85	4.00

[1] Determined by difference.
[2] The ratio of combined tannin to hide substance × 100.
[3] 5 g of leather in 100 ml of distilled water.

The distribution of the samples relative to hide location, for treatment with acid and glucose was similar to that previously described [13], except that each value of deterioration reported is calculated from the average of 11 samples instead of 42. The amounts of sulphuric acid added to the specimens were approximately 0, 1, 2, and 3 percent. After the acid treatment the leather was allowed to dry at room temperature and one-half of the samples were treated in a solution of glucose. The amount of glucose absorbed by the leather was determined by the official method of the American Leather Chemists Association.

The leather was stored at a temperature of 70° F and a relative humidity of 65 percent. Samples for the determination of the tensile strength were taken 0, 6, 12, 18, and 24 months after treatment.

III. RESULTS AND DISCUSSION

The percentages of sulphuric acid and glucose added, the original pH values, and the percentage of glucose and the pH values of the samples after 24 months storage are given in table 2. The percentage change in tensile strength after storage is also given in table 2.

These data show that the addition of glucose had no apparent effect on the original pH value of the leather and that the pH of all the samples containing acid increased after 2 years' storage. It is of further interest to note that the percentage of glucose found in the original samples decreased after storage for 2 years and was the least in the samples having the lowest pH values. Apparently below certain pH values the glucose is decomposed into organic acids, which are not determined by the method of analysis used.

TABLE 2.—*The analysis of the treated leathers and the percentage change in tensile strength*

CHESTNUT

Acid added	Glucose added	Glucose after 24 months	pH original	pH after 24 months	Percentage change in tensile strength for— Age (months) 0	6	12	18	24
0.0	0		3.85	3.97	0.0	0.0	0.0	0.0	0.0
1.18	0		2.99	3.08	−2.4	−5.1	2.3	−2.9	1.1
1.57	0		2.48	2.78	−2.8	−10.4	−8.8	−16.0	−24.8
2.61	0		2.16	2.47	−7.0	−25.6	−28.5	−39.6	−49.0
0.00	5.20	5.14	3.84	4.05	0.0	0.0	0.0	0.0	0.0
1.07	4.80	4.34	2.94	3.15	5.2	3.1	3.5	−2.3	−0.8
1.60	6.00	5.26	2.52	2.81	2.0	−13.6	−0.9	−12.8	−28.1
2.37	5.62	4.02	2.30	2.54	−6.9	−5.9	−38.5	−37.5	−56.3

QUEBRACHO

0.0	0		4.00	4.28	0.0	0.0	0.0	0.0	0.0
0.83	0		2.99	3.26	1.5	−6.0	−13.4	−4.4	−8.0
1.78	0		2.52	2.73	3.5	−1.7	3.4	5.6	−5.5
2.44	0		2.20	2.44	0.2	−21.3	−26.9	−20.0	−18.4
0.00	5.34	5.34	4.09	4.20	0.0	0.0	0.0	0.0	0.0
0.79	5.40	4.84	2.99	3.27	5.8	1.0	1.5	5.2	−4.7
1.60	6.03	5.08	2.57	2.86	−1.8	−7.8	−2.0	3.2	−0.3
2.32	5.86	4.16	2.23	2.51	−2.2	−15.0	−10.2	−12.3	−25.8

The results for the deterioration of the leathers for the 2-year storage period, as a function of the original pH values, are given in figures 1 and 2. The percentage change in tensile strength has been corrected for the change in strength of the control samples containing no added acid, so that the points in the graphs represent the deterioration caused by the acid. The chestnut leather (fig. 1) shows a decided decrease in tensile strength below a pH value of 3. The quebracho leather, figure 2, shows a much greater resistance to deterioration at the lower pH values (below 3) than the chestnut leather. The variation in tensile strength between the leathers containing acid and glucose, and comparable leathers containing similar amounts of acid and no glucose is no greater than the experimental error of the determinations.

IV. SUMMARY

The influence of glucose, added to leather containing sulphuric acid, on the deterioration of the leather during storage was determined by comparing the change with age of the tensile strength of the leather with and without added glucose.

The addition of glucose had no apparent influence on the deteriorating effect of the acid.

The chestnut- and quebracho-tanned leathers showed no deterioration after 2 years' storage at 70° F and 65-percent relative humidity when the pH of the leather was 3 or higher.

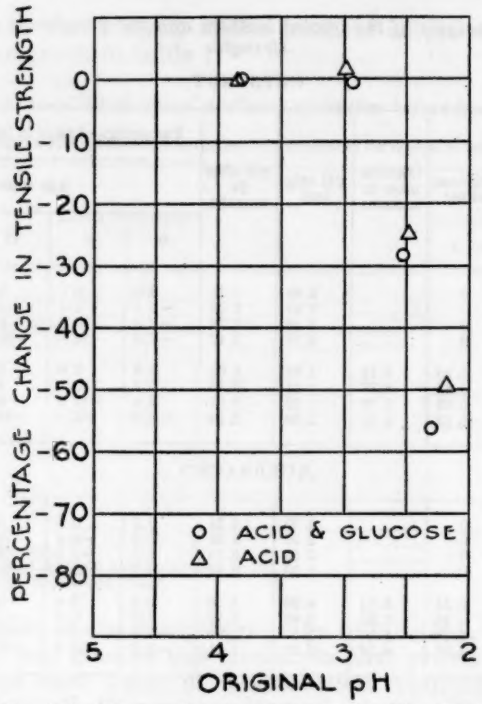

FIGURE 1.—*Results of the 24-month aging tests on lot 25, chestnut-tanned leather, plotted against the* pH *of the leather before aging.*

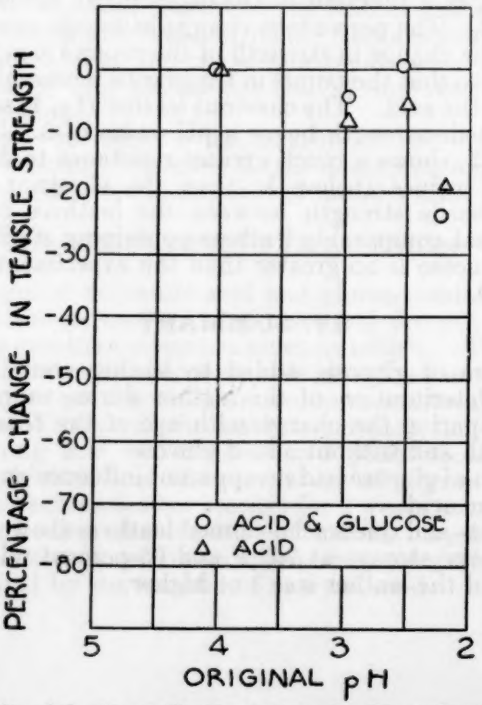

FIGURE 2.—*Results of the 24-month aging tests on lot 26, quebracho-tanned leather, plotted against the* pH *of the leather before aging.*

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WASHINGTON, SEPTEMBER 27, 1935.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP847

Part of Journal of Research of the National Bureau of Standards, volume 15, November 1935

THE PRIEST-LANGE REFLECTOMETER APPLIED TO NEARLY WHITE PORCELAIN ENAMELS

By Irwin G. Priest [1]

ABSTRACT

The Priest-Lange reflectometer is described in detail and the theory of its use given for determining relative apparent reflectance for various spectral distributions of illumination. A method for measuring spectral selectivity of reflectance is also described together with a method for measuring diffuse-plus-specular reflectance as distinguished from diffuse reflectance alone for perfectly polished specimens. The application of the instrument to porcelain enamel samples is illustrated by a detailed account of measurements made on seven typical samples. The method for measuring diffuse-plus-specular reflectance as distinguished from diffuse reflectance is shown to be inapplicable to enamel samples because of their optical imperfections, but measurements of spectral selectivity are shown to give results in close correlation with the colors of the samples observed directly.

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[1] Deceased. From a partially completed report of a cooperative investigation with the McGean Chemical Co. The report was prepared by Mr. Priest in 1929–30; it has been adapted for publication by Deane B. Judd in 1935. The reflectometer has been used more and more widely in the enamel industry since 1930 and is known as the Priest-Lange reflectometer (see, for example, Measurement of Opacity and Color, Am. Enameler 6, 3 (1933)), but no adequate description of it has yet been published.

I. INTRODUCTION

This paper deals with the measurement of the light-reflecting characteristics of glossy, near-white, porcelain enamels by means of the Priest-Lange reflectometer. The measurements reported refer to seven specimens of porcelain enamel, on sheet steel, identified respectively by the numbers 4, 29, 48, 63, 79, 92, and 114. They are considered typical in uniformity and in character of surface. Certain characteristics of the specimens which were far from ideal for the purpose of making highly precise measurements of reflectance will be discussed in turn.

1. FORM OF THE SURFACES

Roughly speaking, the specimens may be called flat, their irregular departures from flatness being of the order of 0.1 mm. However, all were irregularly wavy and so far from plane that (although they give notable specular reflection) the virtual images of objects, using the specimens as mirrors, were either quite unrecognizable or vaguely recognizable only as very indefinite blotches. The departure of the surfaces from planeness caused some inconvenience in making the measurements and necessitated more work than would be required for plane specimens, in order to assure confidence in the results. However, it is not believed that the final results need be essentially less reliable than would those on optically plane specimens.

2. UNIFORMITY OF REFLECTANCE OVER THE SURFACE OF A SINGLE SPECIMEN

The chief object of the measurements was that of finding the reflectance of each of the specimens relative to one of them (48) taken as a standard. Such data can be given without qualification only if the reflectance is uniform over the whole area of each specimen. The total variation of reflectance among the seven different specimens was found to be less than 10 percent of the mean reflectance, while some differed from others by only a few tenths of 1 percent. This problem is typical of those arising in measurement of porcelain enamels. If the variation of reflectance over the area of a given specimen is of the same order of magnitude as that between different samples, it is evident that their grading on the basis of reflectance will have little significance, and may even be misleading. It is also to be remembered that small variations in brightness over a given surface may not be directly perceptible when the change from one part to another is continuous; but will only be detected by bringing the two remote parts into immediate juxtaposition optically. For specimens such as those used in this work, the reflectance at one end might well differ from that at the other by more than 2 percent and yet, if when viewed as a whole the transition from one end to the other were gradual, the surface would still appear to be uniformly bright. The magnitude of this source of error has been estimated by making a detailed analysis of reflectances at different parts of the surface of specimen 48.

3. GLOSS

It should be noted that measuring and specifying the reflectance of glossy surfaces such as these is much less simple than for perfectly diffusing (matt) samples. If an optically smooth enamel is receiving light from an extended source (for example, the sky or the wall of the illumination chamber in the reflectometer described below), and is held at such an angle with the observer's line of sight that his eye receives from it, as from a mirror, regularly reflected light, it will appear brighter than if it is set so that such regularly reflected light does not enter his eye. In the latter case, the brightness is due solely to the light reflected diffusely by the body of the enamel; that is, from light which has penetrated into the body, suffered multiple reflections from the particles within it, and then emerged from it. In the former case, the brightness is due to such diffusely reflected light *plus* the light specularly reflected from the glossy surface. In effect, the observer is viewing two things simultaneously in the same line of sight: (1) The body of the enamel made visible by the light which it diffuses in all directions, and (2) the virtual image of the sky or illuminating surface as seen in a mirror. The total brightness is the sum of the brightnesses associated respectively with these two things. We shall speak of *diffuse brightness* and the *diffuse reflectance* when we refer to the brightness or reflectance due solely to diffuse reflection; and of *specular reflectance* when we refer to the reflectance due solely to the mirror-action of the surface. As will be seen, we have attempted to measure the diffuse reflectance of the enamels separately, and have measured (for some specimens) the diffuse and specular components together. We could not, of course, measure the specular reflectance alone, but we have attempted to compute it from the other measurements.

II. THE REFLECTOMETER

The reflectometer consists essentially of (1) a Martens photometer and (2) an "illumination sphere." The Martens photometer [2] has the following features essential to the present discussion. On looking into the instrument (eye at point E in fig. 1) the observer sees a circular photometric field divided on a diameter. One-half of this field is illuminated by light coming solely from one surface while the other half is illuminated by light coming solely from another surface. By turning the analyzer of the photometer the observer makes the two halves equal in brightness and then computes from such setting ("circular scale in degrees", fig. 1) the ratio of brightness of the two surfaces under comparison.

The illumination sphere is a hollow sphere, the inside surface of which is coated with magnesium oxide. There are open holes in the sphere at top and bottom. Inside, it is illuminated by four[3] small lamps equally spaced around the equatorial belt. These lamps are ordinary 27 candlepower concentrated-filament automobile headlight lamps, commercially rated at 2.1 amperes. On each bulb has been placed a small opaque disk (marked "shadow disks" in fig. 1) which shades the bottom hole of the sphere from the re-

[2] F. F. Martens, Über ein neues Polarisationsphotometer, Phys. Z. 1, 299-303 (1900).
[3] Greater brightness is obtained in some late r models by using ten lamps instead of four.

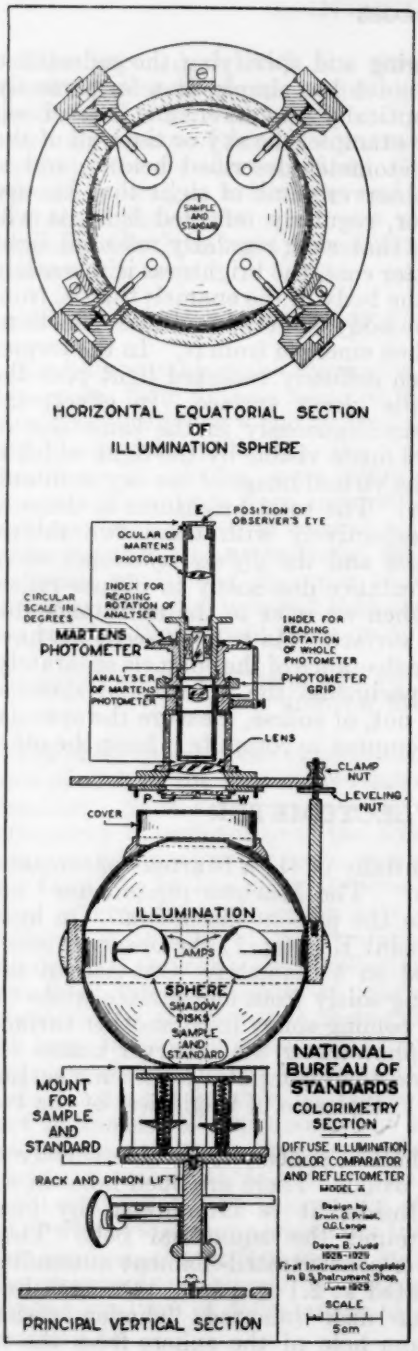

FIGURE 1.—*The Priest-Lange reflectometer.*

The essential details are shown, but for clarity some of the supporting structure is omitted.

spective lamp filament, this area thus being illuminated only by light reflected from the sphere wall.

The Martens photometer is mounted above the sphere with its axis coincident with the vertical axis of the sphere; and the observer with his eye at E looks into the top of the photometer down along this axis.

In the method of interchange[4] the "sample" and "standard" which are to be compared are placed side by side so as to cover respectively the two halves of the hole in the bottom of the sphere as shown in figure 1, and, with plate P and wedge W removed, are imaged respectively in the two halves of the photometer field. By rotation of the stage on which they are mounted the positions of the sample and standard may be reversed. The brightness of the sample relative to the brightness of the standard under the same illumination can thus be measured.

Another method of using the instrument, and indeed the one used exclusively to obtain the present data, is the substitution method. The apparatus is arranged so that a part of the sphere wall at one side of the bottom hole (instead of a part of the area of this hole as in the foregoing paragraph) is imaged in one-half of the photometer field. This is accomplished by means of the glass wedge W. The plane parallel plate P of the same glass compensates for the loss of light caused by the wedge. Both pieces are made of borosilicate crown glass; and the thickness of the plate is equal to the average thickness of the wedge. The positions of the plate and wedge may be reversed, the

[4] H. J. McNicholas, Equipment for Routine Spectral Transmission and Reflection Measurements, BS J. Research 1, 819-829 (1928) RP30. See particularly eq 6 and 35.

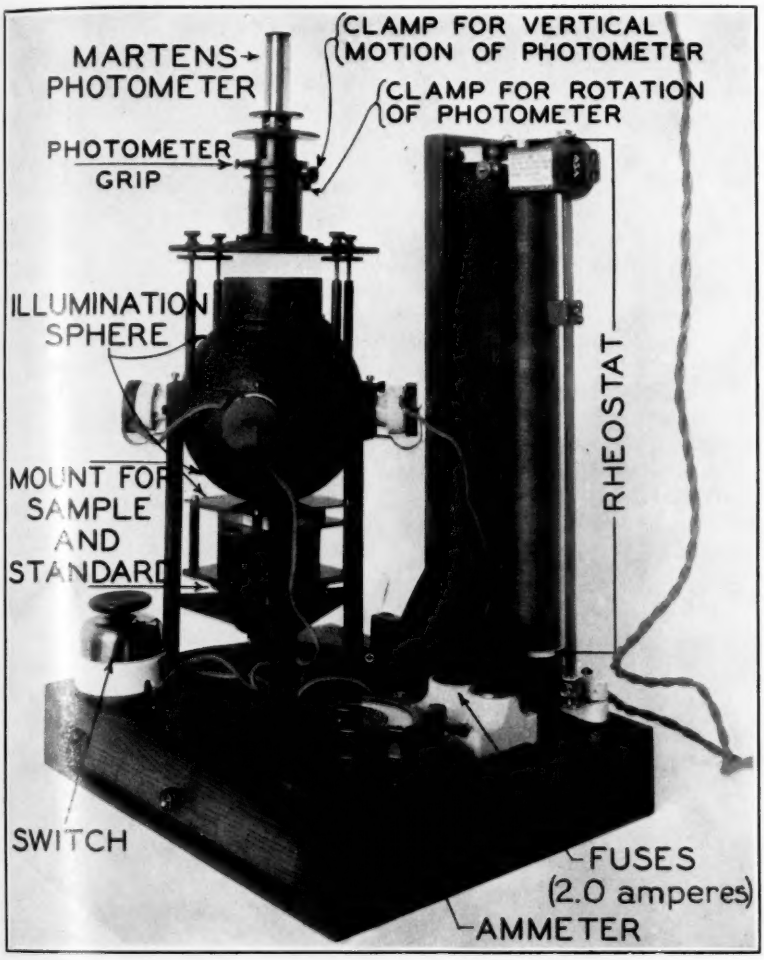

FIGURE 2.—*The Priest-Lange reflectometer and accessory parts.*

The wedge W and plate P shown in figure 1 had not yet been installed when this photograph was taken.

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thin edge of the wedge always being toward the plate. Light from the sphere wall passes through wedge W and illuminates one-half of the photometer field. Light from the specimen at the hole in the bottom of the sphere passes through plate P and illuminates the other half of the field.[5] A sample may now be compared with a standard by the substitution method. Let the standard be placed so as to cover the hole in the bottom of the sphere, and let the photometer field be matched. Let the sample now be substituted for the standard and let the field be matched again. The ratio of the brightness of the sample to the brightness of the standard under the same illumination may be computed from the photometer-scale readings in the two cases, as is explained below.

The spectral distribution of the light used in the measurements is fixed by the nature of the lamp filaments and the current in them, the selective reflectance of the sphere wall, and the ray filter which is inserted between the observer's eye and the photometer ocular. The four filters used are as follows: (1) the "daylight" filter, which is chosen so that the reflectance measurements with it are for artificial sunlight;[6] (2) a blue filter transmitting light of a narrow range of wave length with spectral centroid at about 460 mμ; (3) a similar green filter with spectral centroid at about 540 mμ; and (4) a similar red filter with spectral centroid at about 650 mμ.

The lens placed above the plate and wedge has a twofold purpose; it directs the line of sight towards the desired areas and it controls the condition of focus of the areas viewed. As shown in figure 1, with the end of the photometer close to the lens, the areas viewed are semicircles of 25-mm diameter; and any details of the sample are visible in the photometric field. But, if the photometer be withdrawn from the lens by about 5 cm (see, in fig. 2, clamp for vertical motion of photometer) the area viewed is only of 12-mm diameter and is out of focus so that irregularities in the sample cause little hindrance in making the settings for photometric match.

Figure 2 is a photograph of the reflectometer together with the accessory electrical parts (rheostat, ammeter, and switch), all of which are in series with the four lamps which are themselves in series. The instrument is operated on a regular 110-volt lighting circuit, the desired current (about 1.7 to 1.9 amperes) being set by means of the rheostat. No precise regulation of current is required.

III. METHODS OF MEASUREMENT

1. MEASUREMENT OF REFLECTANCE OF ANY SPECIMEN RELATIVE TO A STANDARD FOR LIGHT OF A GIVEN SPECTRAL DISTRIBUTION

This measurement is accomplished by the substitution method just described. Let a_x be the photometer scale reading (in circular degrees) required for matching the two halves of the photometer field when the sample is in place, and let a_s be a similar reading referring to the standard (which may be, for example, magnesium oxide or another

[5] It was found desirable in 1933 to remove plate P because light scattered by dust collecting on its surfaces caused appreciable errors in measuring apparent reflectance relative to magnesium oxide for dark samples. This does not interfere with any use of the instrument described herein.

[6] Sunlight is somewhat yellower than average daylight, but the difference is too small to have any significant effect on measurements of such samples as these.

of the specimens, say specimen 48). From the theory of the Martens photometer:

$$B_x/B_s=(\tan^2 a_x)/(\tan^2 a_s) \quad (1)$$

where B_x and B_s are, respectively, the brightness of the specimen and standard when they are under the same illumination. This ratio is the apparent reflectance of the specimen relative to the standard for the prescribed type of illumination and angle of view. By making

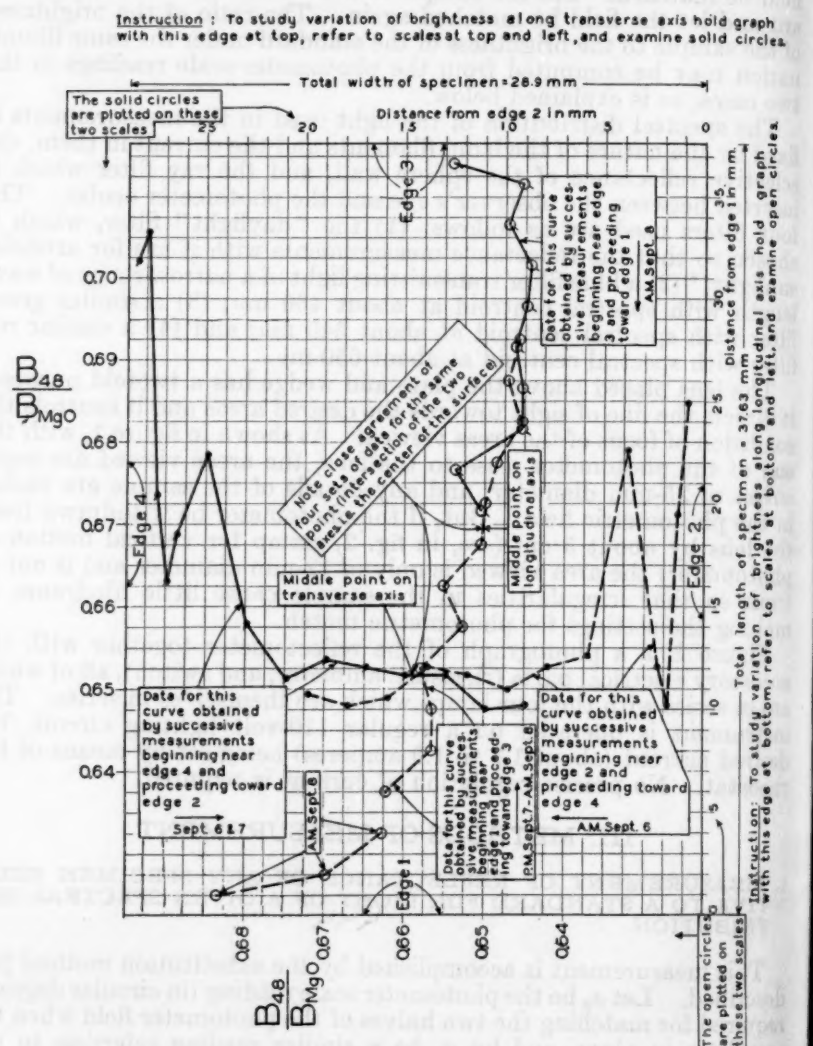
Instruction : To study variation of brightness along transverse axis hold graph with this edge at top, refer to scales at top and left, and examine solid circles.
Total width of specimen = 28.9 mm
The solid circles are plotted on these two scales
Distance from edge 2 in mm
25
20
15
10
5
0
Edge 3
Edge 4
Edge 2
Edge 1
Data for this curve obtained by successive measurements beginning near edge 3 and proceeding toward edge 1
A.M. Sept. 8
Note close agreement of four sets of data for the same point (intersection of the two axes i.e. the center of the surface)
Middle point on longitudinal axis
Middle point on transverse axis
Data for this curve obtained by successive measurements beginning near edge 4 and proceeding toward edge 2
Sept. 6 & 7
A.M. Sept. 8
Data for this curve obtained by successive measurements beginning near edge 1 and proceeding toward edge 3
P.M. Sept. 7 - A.M. Sept. 8
Data for this curve obtained by successive measurements beginning near edge 2 and proceeding toward edge 4
A.M. Sept. 6
B_{48}/B_{MgO}
0.70
0.69
0.68
0.67
0.66
0.65
0.64
Distance from edge 1 in mm.
Total length of specimen = 37.63 mm
Instruction: To study variation of brightness along longitudinal axis hold graph with this edge at bottom, refer to scales at bottom and left, and examine open circles.
The open circles are plotted on these two scales

FIGURE 3.—*Variation of reflectance over the surface of specimen 48.*

the observation with different ray filters over the ocular of the photometer, such brightness ratios may be determined for different spectral distributions of light. It was in this manner that the data shown in figures 3 and 5 and by crosses in figure 4 were obtained; these data are discussed in section V.

2. MEASUREMENT OF SPECTRAL SELECTIVITY OF REFLECTANCE

The theory of the determination of spectral selectivity of reflectance is similar to the above but somewhat less simple. The definition of reflectance is:

$$\frac{\text{Luminous flux proceeding from the specimen}}{\text{Luminous flux incident on the specimen}}$$

or, in other words, the ratio of the quantity of light reflected from the specimen to the light incident on it. This ratio is, in general, dependent upon the wave length of the light in question; and the data show how the reflectance varies with the wave length.

The selectivity data presented in this report are given in terms of apparent reflectance in a direction perpendicular to the surface of the specimen for completely diffused illumination. We designate this particular apparent reflectance as R. The meaning of R may be

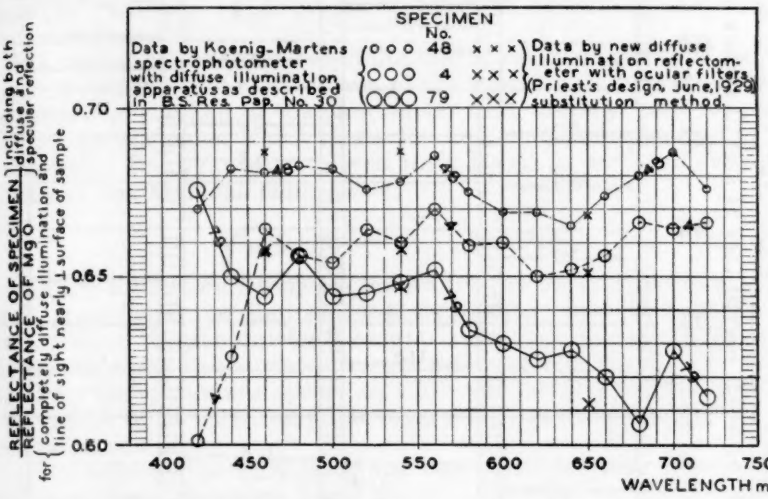
SPECIMEN No.
Data by Koenig-Martens spectrophotometer with diffuse illumination apparatus as described in B.S. Res. Pap. No. 30
○○○ 48 ××× 4 ○○○ 79 ×××
Data by new diffuse illumination reflectometer with ocular filters (Priest's design, June, 1929) substitution method.
REFLECTANCE OF SPECIMEN (including both diffuse and specular reflection)
REFLECTANCE OF MgO
for { completely diffuse illumination and line of sight nearly ⊥ surface of sample
0.70
0.65
0.60
400
450
500
550
600
650
700
750
WAVELENGTH mμ

FIGURE 4.—*Spectral reflectance of specimens 4, 48, and 79 relative to magnesium oxide.*

made more definite by the following illustration of the ideal conditions for its determination.

Assume a hollow sphere such that the brightness of any small element of the inside surface viewed from any point is equal to the brightness of any other element viewed from any point. Let a specimen whose reflectance is to be measured be substituted for a small element of this surface. Then the apparent reflectance of this specimen for a given angle between the line of sight and the normal to the specimen surface is the reflectance which a completely diffusing specimen would need have in order that its brightness should equal the brightness of the given specimen when illuminated and viewed under the same conditions.

Under the ideal condition of completely diffused illumination we would have

$$R = B'_x / B'_e$$

where B'_x is the brightness of the specimen viewed in a direction normal to its surface, and B'_e is the brightness of the sphere wall.

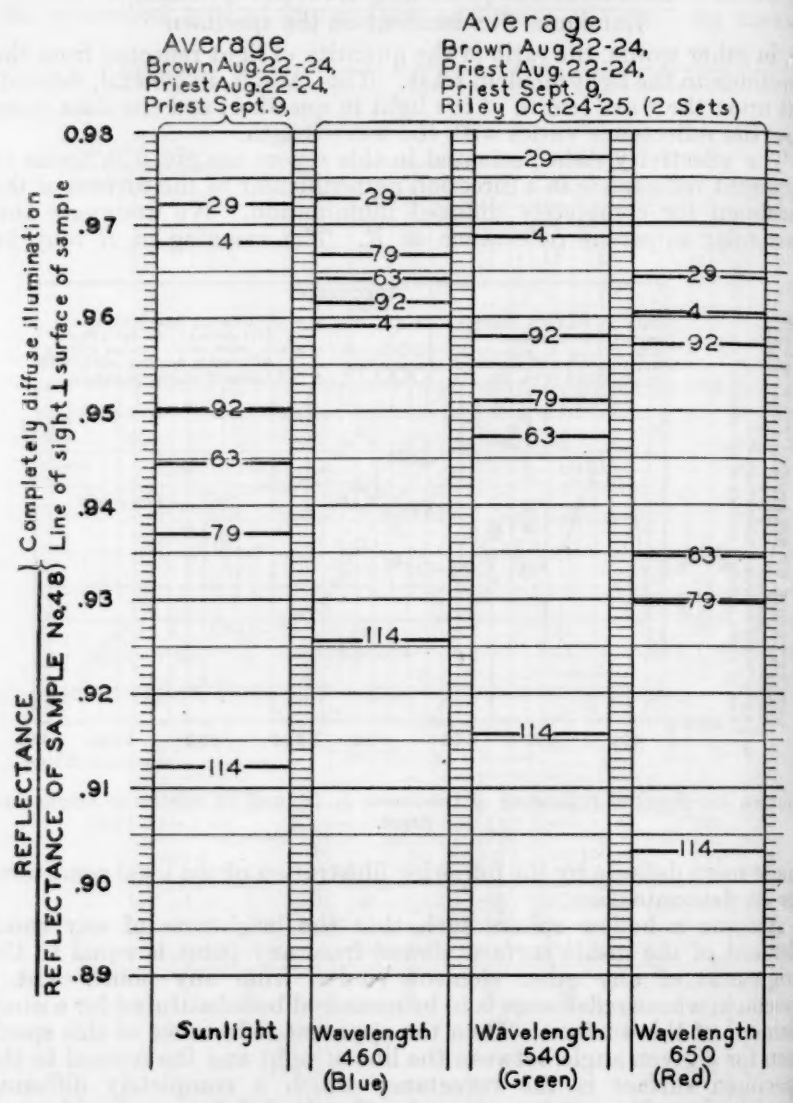

FIGURE 5.—*Reflectance of other specimens relative to specimen 48.*

Of course, the actual apparatus (fig. 1) used to obtain the results reported here does not fully realize the ideal condition of completely diffused illumination. Very little light comes to the sample from the viewing hole; and the sphere wall, itself, viewed from the sample is

not equally bright over its entire surface; furthermore, the lights with their shadow disks introduce slight irregularities.

Therefore, instead of the simple equation, $R=B'_x/B'_c$, we have in practice with this reflectometer the analogous equation:

$$R=K_x(B_x/B_c), \tag{2}$$

where K_x is chiefly a constant of the apparatus measuring, for light of a given spectral-energy distribution, how much the brightness of the observed spot fails to be representative of the average brightness of the whole sphere. K_x also depends somewhat on the diffusing properties of the sample. It would be possible to determine the constant, K_x, as a function of wave length, but this has been deemed unnecessary for our present purpose since from the construction of the sphere it may be seen that K_x is essentially independent of wave length. The purpose of the selectivity measurements is merely to report ratios of the type R_1/R_2, where R_1 and R_2 are respectively the values of R for wave lengths λ_1 and λ_2 (or for spectral distributions of energy designated as 1 and 2). It is obvious that K_x will be eliminated in taking such a ratio.

Let us now consider the determination of ratios of this type for any given specimen. Let a small area of the sphere wall near the bottom be imaged in the half of the photometer field which is dark for $a=0$; and let the specimen which closes the bottom hole be imaged in the other half. For light of any given wave length λ_1 we have, from the theory of the Martens photometer,

$$(B_x/B_c)_1=(\tan^2 a_1)/(\tan^2 (a_0)_1) \tag{3}$$

where the subscripts 1 indicate values for the particular wave length used, λ_1, a_1 being the photometer-scale reading required to make the two halves of the photometer field match and $(a_0)_1$ the like scale reading for match when two surfaces known to be equally bright are substituted for the sphere and specimen, while the observer and the photometer and all of its attached parts except the sphere remain as in the determination of a_1.

If we consider measurements for two wave lengths, λ_1 and λ_2 we will have, from equations 2 and 3

$$\frac{R_1}{R_2}=\frac{(\tan^2 a_1)/(\tan^2 (a_0)_1)}{(\tan^2 a_2)/(\tan^2 (a_0)_2)}, \tag{4}$$

or, if it is arranged that the sphere wall is imaged in the half of the photometer field which is dark for $a=90°$ and the specimen is in the other half, we have cotangents instead of the tangents in eq 4.

In the present report we deal with values of R defined as follows:

R_b is R for wave length 460 mμ.
R_g is R for wave length 540 mμ.
R_r is R for wave length 650 mμ.
R_m is the mean of R_b, R_g, and R_r.
R_s is R for sunlight.

We report values of the following ratios for each of the seven specimens: R_b/R_m, R_g/R_m, R_r/R_m; R_b/R_s, R_g/R_s, R_r/R_s (illustrated in figs. 6, 7, and 8 and discussed in section V).

The first three ratios may be computed according to relations of the form:

$$\frac{R_b}{R_m}=\frac{3\ (\tan^2 a_b)/(\tan^2 (a_0)_b)}{\dfrac{\tan^2 a_b}{\tan^2 (a_0)_b}+\dfrac{\tan^2 a_g}{\tan^2 (a_0)_g}+\dfrac{\tan^2 a_r}{\tan^2 (a_0)_r}} \tag{5}$$

or from similar equations involving cotangents instead of tangents, depending on which side of the photometer field refers to the sphere wall and which to the specimen. The second three ratios may be computed according to relations of the form:

$$\frac{R_b}{R_s}=\frac{(\tan^2 a_b)/(\tan^2 (a_0)_b)}{(\tan^2 a_s)/(\tan^2 (a_0)_s)} \tag{6}$$

or the analogous cotangent form dependent on the conditions just mentioned.

The constants $(a_0)_b$, $(a_0)_g$, $(a_0)_r$ were determined by a separate experiment as follows:

The Martens photometer and the stage upon which it is mounted, together with the lens and the wedge and plate (W and P, fig. 1), were removed as a unit from the position shown in figure 1 and mounted over another illumination sphere similar to that shown in figure 1, but arranged so that both halves of the photometer field were illuminated by light from the sphere wall, one half receiving light from a spot to the left of the bottom pole of the sphere while the other half received light from a spot to the right of this pole. With the appropriate filter (blue, green, or red) to determine $(a_0)_b$, $(a_0)_g$, or $(a_0)_r$ over the ocular, and with the photometer field oriented with respect to the observer's right and left just as in the setting of angle a for the reflectance measurements, the two halves of the field were matched by turning the photometer analyzer, and the photometer scale reading noted. The whole illumination sphere was then rotated and displaced under the photometer (all things else remaining undisturbed) so as to image in the right half of the photometer field the part of the sphere wall formerly imaged in the left half and vice versa. The two halves of the photometer field were again matched by turning the photometer analyzer, and the photometer scale reading was noted. The mean of the two scale readings just mentioned was taken as equal to $(a_0)_b$, $(a_0)_g$, or $(a_0)_r$, depending upon the ocular filter used in making the photometric matches. Each value in table 1 is a mean resulting from 100 separate settings of the angle a.

TABLE 1.—*Cotangents squared of* $(a_0)_b$, $(a_0)_g$, *and* $(a_0)_r$ *for two observers*

For Wedge in Field Dark for $a=0°$

	$\cot^2 (a_0)_b$	$\cot^2 (a_0)_g$	$\cot^2 (a_0)_r$
Priest	1.008	1.002	1.008
Riley	1.017	1.013	1.014

For Wedge in Field Dark for $a=90°$

	$\cot^2 (a_0)_b$	$\cot^2 (a_0)_g$	$\cot^2 (a_0)_r$
Priest	1.019	1.013	1.026
Riley	1.026	1.027	1.026

It appears from table 1 that in reducing observations of spectral selectivity (particularly for observer Riley) we could introduce the simplifying equation:

$$(a_0)_b=(a_0)_g=(a_0)_r$$

without introducing any error greater than that necessarily inherent in the result from other causes (that is, a few tenths of 1 percent). If this simplifying equation be introduced into eq 5, the much simpler form for computation, eq 7, results:

$$\frac{R_b}{R_m}=\frac{3\tan^2 a_b}{\tan^2 a_b+\tan^2 a_g+\tan^2 a_r}. \tag{7}$$

This may be used for all cases except those in which we hope to reduce the uncertainty in the final result to less than 1 percent of the reflectance.

In general, determination of $(a_0)_b$, $(a_0)_g$, and $(a_0)_r$ need not involve a separate illumination sphere. All that is required is a surface of nearly uniform brightness so arranged that the two observed spots can be interchanged without disturbing the rest of the system.

3. MEASUREMENT OF DIFFUSE-PLUS-SPECULAR REFLECTANCE AS DISTINGUISHED FROM DIFFUSE REFLECTANCE ALONE

If a plane mirror (for example, a plane polished sheet of silver or a plane polished plate of black glass) be placed in the position of the sample or standard (on the stage just below the hole in the bottom of the sphere) with its surface perpendicular to the axis of the photometer, the half of the photometer field in which the hole is imaged will be dark because the virtual image of the dark hole in the top of the sphere will then alone appear in this field. If a diffusing surface (instead of a mirror) be placed in this position, the same half of the field will be illuminated by the light diffusely reflected from this surface in the direction perpendicular to it. If the diffusing surface be tilted so that the perpendicular to it makes an angle of about 3 to 4° with the axis of the photometer, its brightness will not be sensibly changed, provided that its distance from the bottom of the sphere is not increased to more than 1 mm. (By actual test, increasing the distance of the surface from the sphere bottom from 0 to 1.0 mm decreases the brightness by 0.35 percent; increasing the distance from 0 to 1.5 mm decreases the brightness 0.8 percent.[7]) If, on the other hand, a mirror be placed in the sample position with the perpendicular to its surface making an angle of 3 or 4° with the photometer axis, one will see in the photometer field a virtual image of a part of the sphere wall near the top of the sphere. The brightness of the virtual image will be equal to the brightness of the sphere wall multiplied by the reflectance of the mirror for normal incidence. (The reflectance of a mirror for normal incidence is sensibly equal to its reflectance for angle of incidence equal to 4°.) If now, instead of either a perfect diffusor or a perfect mirror, we have to deal with a specimen which reflects diffusely from the body of its material but is coated with

[7] The decrease in brightness to be expected has been computed from the geometry of the apparatus and found to depend importantly on the size of the sample hole, thus:

Distance, sample to sphere bottom, mm	0.5	1.0	1.5	2.0
Decrease for 3-cm sample hole as in apparatus used by Priest, percent	0.10	0.43	1.00	1.73
Decrease for 2-cm sample hole as in some more recent models, percent	0.24	0.98	2.20	3.86

These computed results are in good agreement with Priest's experimental findings, but at the same time they indicate that the brightness of the sample will be noticeably decreased in some of the recently built reflectometers by a withdrawal of as much as 1.0 mm (D.B.J., July 1935.)

a vitreous glaze which reflects as a mirror we have the following situation:

First, the specimen being placed with its surface perpendicular to the axis of the photometer, the brightness of the photometer field will be due solely to light reflected diffusely by the specimen, for no specularly reflected light will enter the photometer.

Second, the specimen being placed so that the perpendicular to its surface makes an angle of about 3 or 4° with the axis of the photometer, the brightness of the photometer field will be due to light reflected diffusely plus light reflected specularly; and, since the brightness due to the diffuse component is not affected by this small angular change in position of the surface, the brightness in this case will be greater than with the surface strictly perpendicular to the photometer axis.

For certain specimens, we have determined for both of the above-mentioned positions, the brightness ratio, B_x/B_{MgO}, where B_x is the brightness of the specimen, and B_{MgO} is the brightness of magnesium oxide (see eq 1). To interpret and consider the results with the least possible confusion, let us adopt symbols as follows:

B_c is the brightness of the unshaded magnesium-oxide coated sphere wall near either the top or the bottom of the sphere. (For simplicity, and without introducing any appreciable error, we assume that the brightness near the bottom is equal to the brightness near the top.)

$(B_x)_d$ is the brightness of the specimen due to diffuse reflection in the direction perpendicular to its surface. This is the brightness of the specimen in the direction of the vertical axis of the sphere when its surface is perpendicular to this axis.

$(B_x)_{d+s}$ is the brightness of the specimen due to both diffuse and specular reflection. This is the brightness of the specimen in the direction of the vertical axis of the sphere when it is tilted so that its surface regularly reflects light from the sphere wall (near the hole in the top of the sphere) along this axis.

We then have the following apparent reflectances relative to magnesium oxide, each of which may be measured by means of the Martens photometer:

$$r_d=(B_x)_d/B_{MgO}, \tag{8}$$

and

$$r_{d+s}=(B_x)_{d+s}/B_{MgO}; \tag{9}$$

and we may also measure the brightness ratio, B_{MgO}/B_c, which from eq 2 is equal to R_{MgO}/K_{MgO}. Let ρ be the specular reflectance of the specimen surface for normal (or nearly normal) incidence. We then have obviously,

$$(B_x)_{d+s}=(B_x)_d+\rho B_c. \tag{10}$$

Substituting eq 10 in eq 9, we have:

$$r_{d+s}=\frac{(B_x)_d+\rho B_c}{B_{MgO}}. \tag{11}$$

Reducing eq 11 and substituting eq 2 and 8, we have:

$$r_{d+s}=r_d+\rho(K_{MgO}/R_{MgO})$$

Solving for ρ, we have:

$$\rho=(R_{MgO}/K_{MgO})(r_{d+s}-r_d). \tag{12}$$

We desire to know r'_{d+s}, the value which r_{d+s} would assume if (instead of the actual illumination sphere which we use) the sphere were such as to make B_{MgO}/B_c equal to R_{MgO}, the apparent reflectance

of magnesium oxide for completely diffused illumination and line of sight perpendicular to the surface, that is, such as to make $K=1$ for magnesium oxide. In such a sphere, we would have:

$$r'_{d+s}=r'_d+\rho/R_{MgO}$$

where r'_d for this ideal sphere is analogous to r_d in our actual sphere. But we may assume for enamel surfaces r'_d equal to r_d within experimental error and then we have:

$$r'_{d+s}=r_d+\rho/R_{MgO}$$

or

$$r'_{d+s}=r_d+(r_{d+s}-r_d)/K_{MgO} \tag{13}$$

It is to be recalled now that r_{d+s} and r_d are directly measured quantities. For the present specimens, the difference, $r_{d+s}-r_d$, has been found experimentally to vary only between 0.014 and 0.034. In the actual apparatus used to measure r_d and r_{d+s}, the value of R_{MgO}/K_{MgO} has been experimentally found to be about 0.94; the value of R_{MgO} is known to lie between 0.97 and 0.98; hence $1/K_{MgO}$ is equal to about 0.96. Since we shall not attempt to report r'_{d+s} to more than three decimal places, it is obvious from eq 13 that an uncertainty of 2 percent in $1/K$ is negligible and, for present purposes, we may take $1/K$ as 0.96 without further discussion not only for magnesium oxide but also for these enamel specimens whose diffusing properties are similar.

It is also worth noting that the accuracy with which r'_{d+s} is determined depends almost entirely on the accuracy with which r_{d+s} is measured. This may be seen by rewriting eq 13 in the form:

$$r'_{d+s}=r_{d+s}(1/K)+r_d(1-1/K).$$

The values of r_d, r_{d+s}, ρ, and r'_{d+s} for specimens 4, 48, and 79 are given in table 2, and are discussed in section V.

The values plotted by crosses in figure 4 have been computed by eq 13, taking $1/K=0.96$. As a practical matter, however, it may be noted that, with these specimens, we could take r'_{d+s} equal to r_{d+s} instead of computing by eq 13, without introducing any error greater than the uncertainty in the data.

IV. STANDARD FOR REFLECTANCE MEASUREMENTS

The magnesium oxide used as a standard, to which the reflectance of the specimens is referred (in figs. 3 and 4, and table 2), is prepared by burning metallic magnesium so that the magnesium oxide "smoke" is deposited on a surface held over the flame (about 10 cm from the burning metal).[8] Successive layers are deposited to such a thickness that increasing the thickness produces no further change in reflectance. The critical thickness is about 0.5 mm. The apparent reflectance [9] of such a deposit for completely diffused illumination with line of sight perpendicular to the surface may be taken as between 0.97 and 0.98. (With the present apparatus in which the angular distribution of the illumination departs from the condition of complete diffusion chiefly by reason of the viewing hole at top of

[8] Detailed instructions are given in Letter Circular of the National Bureau of Standards LC395, Preparation and Colorimetric Properties of a Magnesium Oxide Reflectance Standard.

[9] When the sample is so thick that its reflectance depends on the material rather than its dimensions, the term "reflectivity" is often substituted for reflectance (J. Opt. Soc. Am. and Rev. Sci. Instr. **10**, 178 (1925); J. Research NBS **13**, 282 (1934)). The expression here might therefore be "apparent reflectivity." (D.B.J., July 1935.)

the sphere, the apparent reflectance of a thick layer of magnesium oxide with line of sight perpendicular to the surface is lower than this by a few tenths of 1 percent, and may be taken as about 0.97.) We shall assume $R_{MgO}=0.975$ for $\lambda=560$ mμ and for sunlight.

As to selectivity with respect to wave length, the reflectance for blue and green is slightly greater than for red; but the departure from the mean value over the wave-length range 460 to 650 mμ is nowhere greater than 0.5 percent, as is indicated by the following data by Priest and Riley: [10] $R_b/R_m=1.0044$, $R_g/R_m=1.0010$, $R_r/R_m=0.9946$. Assuming R for wave length 560 mμ as 0.975, we estimate: $R_b=0.979$, $R_g=0.976$, $R_r=0.970$.

V. RESULTS OF THE MEASUREMENT OF SEVEN PORCELAIN ENAMELS

1. VARIATION OF REFLECTANCE OVER THE SURFACE OF SPECIMEN 48

The specimen was mounted on a stage actuated by a micrometer screw so that it could be moved by measured steps across the field of view in a direction perpendicular to the line of sight, the plane of the specimen surface being in focus in the photometer field. By this device the images of the various points of the surface were brought to coincidence with the division line in the photometer field.

Each point plotted in figure 3 is derived from the mean of ten independent settings of brightness match for the corresponding point on the specimen. These ten brightness matches are not made in immediate succession. On the contrary, the order of observations was as follows: First, one setting of brightness match was made for the point nearest an edge, then one setting for the next nearest point, and so on, taking points in order until the point nearest the opposite edge was reached. This order of observation was then repeated nine times, giving the ten independent settings from which each of the plotted values was obtained. The ratio B_{48}/B_{MgO} was computed by eq 1. The solid circles refer to observations taken along the transverse axis; the open circles, to the longitudinal axis.

It may be concluded from figure 3 that the reflectance along the transverse axis is sensibly constant for a distance of 6 or 7 mm on both sides of the midpoint. Outside of these limits (that is, for strips about 6 or 8 mm wide adjoining the lateral edges) the measured reflectance tends to be notably higher. Near the edges, values higher than the central values by as much as 10 percent have been obtained.

Along the longitudinal axis there is also a tendency to relatively high values near the edges; but the distribution is less symmetrical than along the transverse axis, values to the side of the center toward edge 1 (also near the center) being systematically higher than values for symmetrical points on the other side of the center. However, the region extending about 4 or 5 mm on both sides of the center may be considered as sensibly constant (taking into account the uncertainty of the measurements).

[10] I. G. Priest and J. O. Riley, The Selective Reflectance of Magnesium Oxide, J. Opt. Soc. Am. 20, 156 (1930).

In general it is difficult to interpret strictly the significance of the measurements near the edges where the enamel is usually piled up to form what is known as the "bead." The high values may be partly due to "high lights" occasioned by specular reflection from the curved surfaces of the "bead", and partly to increased thickness of enamel at the "bead." However, near the edges a photometric field unsatisfactory for precise measurements is obtained; the division line in the photometer field does not disappear when one attempts to match the two halves of the field. The chief conclusion we draw from these measurements is that precise and significant measurements to serve for intercomparing the several specimens cannot be made near their edges.

2. SPECTRAL REFLECTANCE OF SPECIMENS 4, 48, AND 79 RELATIVE TO MAGNESIUM OXIDE

The circles in figure 4 represent apparent spectral reflectance relative to magnesium oxide obtained on the König-Martens spectrophotometer with the illumination chamber used in routine measurements at the Bureau.[11] The approximation to completely diffused illumination is so close that the measurements may be taken as for completely diffused illumination.

The crosses refer to data taken on the reflectometer here described, and, strictly speaking, are not precisely for the wave lengths at which they are plotted, but rather represent the average reflectance for a small range of wave lengths on both sides of the plotted value. The values of apparent reflectance have been corrected so as to refer to completely diffused illumination. They are the values of r'_{d+s} given in table 2 to be discussed presently.

All values may be considered as for the center of the specimen, although the measurements by the König-Martens spectrophotometer were actually for points perhaps 7 mm from the center.[12] The agreement between the results by the two instruments is seen to be within experimental uncertainty.

3. DIFFERENCE BETWEEN DIFFUSE-PLUS-SPECULAR REFLECTANCE AND DIFFUSE REFLECTANCE ALONE

Data illustrating the difference between diffuse-plus-specular reflectance and diffuse reflectance alone for specimens 4, 48, and 79 are shown in table 2.

From these data has been computed the average specular reflectance for normal incidence (ρ as given by eq 12), which is 0.023. From Fresnel's reflection formula one would expect ρ for a plane polished surface of glass of refractive index 1.53 to be 0.044. As a matter of

[11] H. J. McNicholas, Equipment for Routine Spectral Transmission and Reflection Measurements, BS J. Research, 1, 793 (1928) RP30. The spectral reflectance measurements on the enamels were made by Mabel E. Brown.

[12] Previous spectrophotometric measurements made near the edges of the samples were discarded. However, these previous data do not differ significantly from those illustrated. A consideration of all the data indicates:

(1) That most of the minor and seemingly erratic variations are probably not real. This is to be expected since the uncertainty in most of the values illustrated is probably as great as 0.01 and even more toward the ends of the spectrum. This is particularly true at 460 mμ for specimen 4, the true value of which is probably about 0.65. However, the low values at 540 and 580 mμ relative to the respective values at 560 mμ were consistently obtained throughout.

(2) That the relatively strong absorptions of specimen 4 in the violet and of specimen 79 in the red are real. The coincidence between the colorimetric results computed from the illustrated data and the colors of the samples as judged by direct examination is considered later. (K.S.G., Aug. 1935.)

fact we have measured ρ for highly polished black glass of this index with this same instrument and have obtained the experimental value of 0.042_5. It may also be noted that McNicholas had previously reported $\rho=0.043$ for this same piece of black glass.[13] For glossy "velox" photographic paper we have also found $\rho=0.045$ with this same apparatus. It is admitted that the values of $(r_{d+s}-r_d)$ given in table 2, and consequently the values of ρ may be individually uncertain by as much as 0.01, or even 0.02; but it is very improbable that they are systematically lower than the true value by as much as 0.02.

TABLE 2.—*Comparison of diffuse-plus-specular reflection with diffuse reflection alone*

Quantity [1]	Specimen	48			4			79		
	Ocular filter Spectral centroid	Blue 460	Green 540	Red 650	Blue 460	Green 540	Red 650	Blue 460	Green 540	Red 650
r_{d+s}		0.688	0.689	0.669	0.658	0.659	0.653	0.659	0.648	0.613
r_d		.661	.658	.647	.633	.639	.619	.636	.626	.599
$r_{d+s}-r_d$		.027	.031	.022	.025	.020	.034	.023	.022	.014
$0.96\ (r_{d+s}-r_d)$		.026	.030	.021	.024	.019	.033	.022	.021	.013
$r'_{d+s}=r_d+(r_{d+s}-r_d)/K_{MgO}$		.687	.688	.668	.658	.658	.652	.658	.647	.612

[1] See eq 13.

When one considers the known waviness of the surfaces of these specimens and the unknown degree of polish of such surfaces, the apparently low value of ρ is seen to be not a matter to cause astonishment. It should be emphasized that our method of finding ρ tacitly assumes that the surface is optically plane, whereas these surfaces come far from fulfilling this condition.

It may be concluded, therefore, that values of r_d do not represent diffuse reflectance solely from the body of the enamel; a small part of the diffusely reflected light comes from the surface itself.

4. APPARENT REFLECTANCE OF SPECIMEN 48

On the basis of all of our data we adopt the following values of $r_d=(B_{48})_d/B_{MgO}$; see eq 8.

	r_d
For sunlight	0.6576
For $\lambda_e=460m\mu$	.6593
For $\lambda_e=540m\mu$	.6575
For $\lambda_e=650m\mu$	.6461

These relative values may be put on an absolute basis by taking into account the apparent reflectance of magnesium oxide, R_{MgO}, thus:

For sunlight	$0.6576\times0.975=0.641$
For $\lambda_e=460m\mu$	$.6593\times .979= .645$
For $\lambda_e=540m\mu$	$.6575\times .976= .642$
For $\lambda_e=650m\mu$	$.6461\times .970= .627$

[13] H. J. McNicholas, Absolute Methods in Reflectometry, BS J. Research 1, 53 (1928).

The corresponding values for apparent diffuse-plus-specular reflectance are less accurate. However, approximate values (subject to an error probably less than 0.01) may be obtained by adding 0.023 to the corresponding values for diffuse reflectance just given.

In the case of either diffuse-plus-specular reflectance or diffuse reflectance alone, the values for any of the other specimens may be obtained by multiplying the value for specimen 48 by the appropriate relative reflectance taken from figure 5.

5. APPARENT REFLECTANCE OF OTHER SPECIMENS RELATIVE TO SPECIMEN 48

The reflectance of each specimen relative to the reflectance of specimen 48 for completely diffused illumination, with line of sight

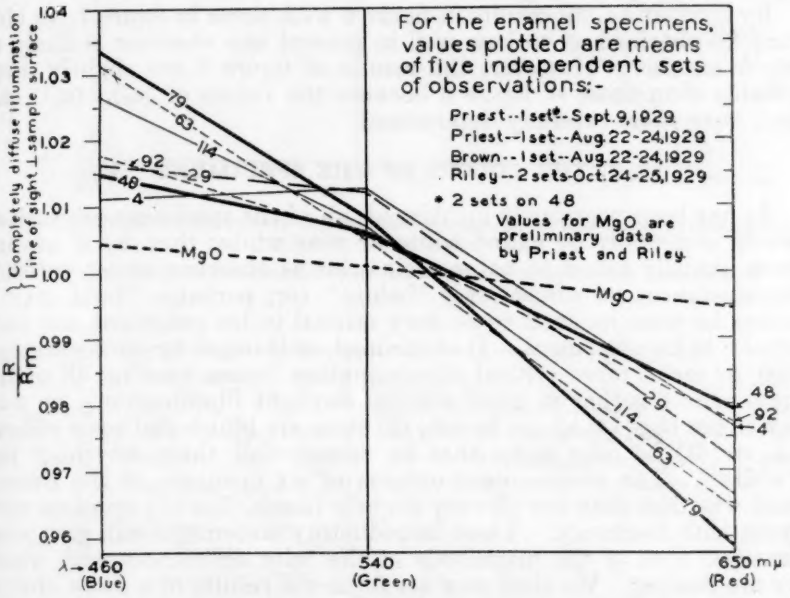

FIGURE 6.—*Spectral selectivity of reflectance by equation 5, mean of all data.*
The three values shown for each specimen are reflectances relative to the mean for that specimen.

perpendicular to the specimen surface, is given by figure 5. The results shown were obtained according to eq 1. The measurements refer to diffuse reflection but these ratios would be sensibly the same for measurements including both diffuse and specular reflection for each specimen relative to specimen 48. Each plotted value is the result of at least 60 settings of brightness match, but no great significance should be attached to relative order of specimens when the difference between them is less than one percent.

It may be noted: (1) that the range of sunlight reflectance in this collection of seven specimens is about 9 percent; (2) that specimen 48 is undoubtedly the lightest and specimen 114 the darkest; (3) that specimen 48 reflects some 2 or 3 percent more than its closest rival, specimen 29; and (4) that specimen 114 falls in a class by itself as notably dark relative to the others.

6. SPECTRAL SELECTIVITY OF THE SPECIMENS

The selective reflectance (selective with respect to wave length) of the specimens relative to specimen 48 may be inferred from figure 5. However, as has been shown in section III above, we can measure and express the selectivity of reflectance on an absolute basis, without taking into account the reflectance of any other specimen or standard material.

The data on spectral selectivity of reflectance for these seven specimens are exhibited in figures 6, 7, and 8. The interpretation and essential significance of these figures may be readily seen from the figures themselves and from the description of the method of measurement given in section III. The results shown in figures 6 and 7 were obtained by the method indicated by eq 5; those shown in figure 8, by eq 6.

By comparing the results in figure 6 with those in figure 7, an idea may be obtained as to how well in general one observer is likely to check another. However, the results of figure 7 are slightly more reliable than those of figure 6 because the values of $(a_0)_b$, $(a_0)_g$, and $(a_0)_r$ were more carefully determined.

7. THE COLORS OF THE SPECIMENS

As has been previously mentioned, all of the specimens are such as would commonly be called white or near white; that is, if anyone were casually asked to name their color as observed under ordinary circumstances he would reply "white" (or, perhaps, "light gray") unless he were inclined to be very critical in his judgment and very precise in his statement. If so inclined, or if urged by cross-examination to make more critical discrimination (when viewing all of the specimens together in good average daylight illumination), he may say either that (1) all are bluish, (2) some are bluish and some yellowish, or (3) he may insist that he cannot call them anything but "white". The predominant opinion of six members of the Bureau staff was that they are all very slightly bluish; but the opinions were given with hesitancy. These introductory statements will give some practical idea of the magnitude of the color differences with which we are dealing. We shall now set forth the results of a more critical examination of the specimens.

(a) THE COLORS OF SPECIMENS 4, 48, AND 79, COMPUTED FROM DATA ON SPECTRAL REFLECTANCE

The basic ideas on which the computation of these color specifications from spectral reflectance depends will first be briefly set forth. The color of any one of these specimens (in sunlight) may be matched by a mixture of sunlight and homogeneous light of some wave length selected from the spectrum. The particular wave length which it is found requisite to select in order to match the color of the specimen in this manner is called the "dominant wave length" (Λ) of that specimen. In order to match the color of the specimen it is necessary to mix the homogeneous light and the sunlight in a certain particular ratio. This ratio is specified by the purity p, purity being defined as the ratio of the brightness of the homogeneous component of the mixture to the brightness of the mixture itself.

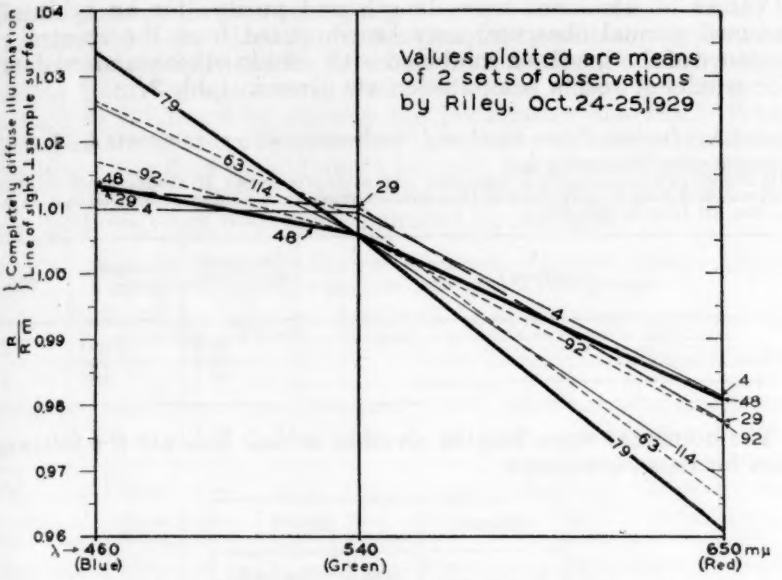

FIGURE 7.—*Spectral selectivity of reflectance by equation 5, most careful determinations by one observer.*

The three values shown for each specimen are reflectances relative to the mean for that specimen.

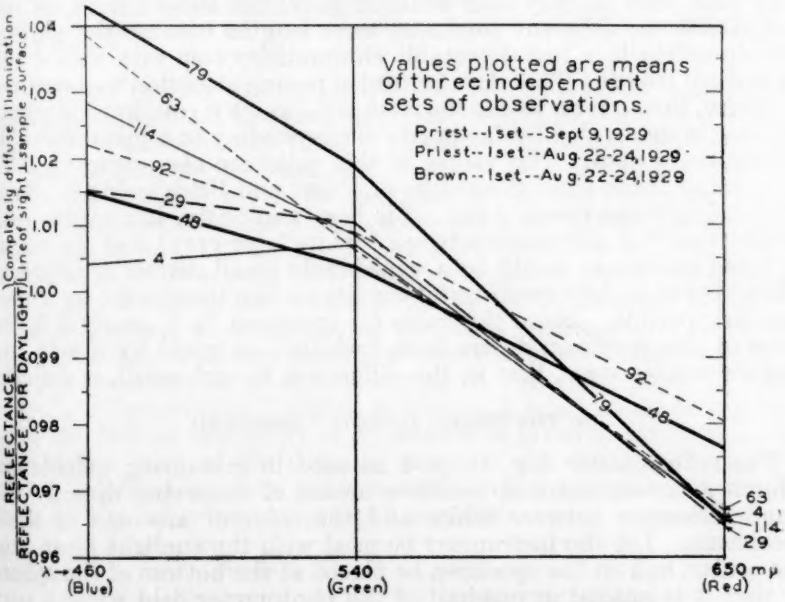

FIGURE 8.—*Spectral selectivity of reflectance by equation 6.*

The three values shown for each specimen are reflectances for blue, green, and red light, each relative to reflectance for sunlight.

Values of dominant wave length and purity (for an arbitrarily assumed normal observer) may be computed from the spectral reflectance of the specimen combined with certain other standard data.[14] The results of such a computation are given in table 3.

TABLE 3.—*Dominant wave length and colorimetric purity of specimens 4, 48, and 79*

[Computed from the following data:
(1) Spectral reflectance relative to magnesium oxide as given in figure 4; (2) absolute selectivity of magnesium oxide as given in figure 6; and (3) OSA standard observer and coordinate system (J. Opt. Soc. Am. and Rev. Sci. Instr. **10**, 230 (1925))].

Specimen	Dominant wave length, λ	Colorimetric purity, p	p/p_0
4	565.4	0.0345	0.73
48	488.4	.0060	.87
79	483.4	.0105	1.78

The dominant wave lengths given in table 3 indicate the following hues for these specimens:

Specimen	Hue
4	Green or yellow-green.
48	Blue or blue-green.
79	Blue or blue-green.

The values of purity, being very small, indicate that the colors are very pale, that is, very near white or gray; but these values are not comparable for different dominant wave lengths because the purities corresponding to a just detectable chromaticity step vary with dominant wave length. Therefore, instead of paying attention to the values of purity, themselves, we use the ratio p/p_0, which is colorimetric purity of the sample divided by the purity corresponding to a just noticeable chromaticity step. The values of this ratio are also given in table 3, p_0 being taken from the results of Priest and Brickwedde.[15] Since this ratio for specimens 4 and 48 is less than unity, it may be concluded that the difference between "white" (or gray) and the colors of these specimens would be a vanishingly small doubtful difference when viewed under experimental conditions like those used by Priest and Brickwedde. Since this ratio for specimen 79 is nearly 2.0, the color of this specimen differs from "white" (or gray) by nearly two just detectable steps, that is, the difference, though small, is definite.

(b) THE COLORS DIRECTLY OBSERVED

The reflectometer (fig. 1), just as used in measuring reflectance, affords a convenient and sensitive means of observing directly the small difference between white and the color of any one of these specimens. Let the instrument be used with the sunlight filter over the ocular, and let the specimen be placed at the bottom of the sphere so that it is imaged in one-half of the photometer field while a part of the sphere wall is imaged in the other half. The important point

[14] These data, together with directions and forms for the computation, are given in J. Opt. Soc. Am. **23**, 359 (1933).

[15] I. G. Priest and F. G. Brickwedde, The Minimum Perceptible Colorimetric Purity as a Function of Dominant Wave Length with Sunlight as Neutral Standard, J. Opt. Soc. Am. and Rev. Sci. Instr. **13**, 306 (1926).

to be emphasized in this arrangement is that one-half of the field is illuminated by light which is identical in quality with the light which falls on the specimen while the other half is illuminated by light reflected from the specimen. The two halves of the field may be matched in brilliance by turning the photometer analyzer. When this has been done it is obvious that the quality difference remaining is nothing other than the difference between the color of the specimen and the color of a strictly nonselective (white or gray) surface of the same lightness when both are illuminated by sunlight.

TABLE 4.—*Hues of the specimens by direct comparison of their colors under artificial sunlight illumination with the color of that illumination*

The comparison was made at equal brilliance in the Martens photometer field with the apparatus shown in figure 1.[a] Results for MgO and $MgCO_3$ under identical conditions are shown for comparison.

Observer	Specimen								
	4	29	48	63	79	92	114	$MgCO_3$	MgO
Judd	Green	Green	Green	Green-blue.	Green-blue.	Green	Green-blue.	Yellow	Yellow?
Gibson	Green	Green	Blue	Blue	Blue	Blue	Blue	Yellow?	Neutral.
Brown	Blue	Blue	Green-blue.	Blue	Blue	Blue	Blue	Pink?	Blue?
Riley	Blue-green.	Blue-green.	Blue-green.	Blue-green.	Blue-green.	Blue-green.	Blue-green.	Red	Neutral?
Blue-green ratio[b]	0.67	0.67	1.0	2.0	2.0	1.5	2.0		
Mean response time (seconds).	14.5	22.0	21.7	14.7	16.7	30.5	11.7	34.0	56.6.

[a] The observer had been specifically requested to report the slightest difference he suspected, however small and doubtful, and say "neutral" or "matched" only when there was no suggestion of difference. The observer adjusted the brilliance match at pleasure while making his decision.

[b] Ratio of number of times the "blue" was used in naming the hue to the number of times the word "green" was used.

With this viewing arrangement a number of observers have looked at the specimens and have named, or attempted to name, their colors. The results are shown in table 4. Results on magnesium carbonate and magnesium oxide obtained at the same time and under the same conditions are also given for comparison. The oxide is so nearly neutral that observations such as these fail utterly to give any certain indication of hue, but the selectivity of reflectance is such as to tend to make the oxide appear blue. The carbonate is perceived as doubtfully yellowish or reddish, which is in accord with the slight selectivity of its reflectance as measured on this same instrument. Inspection of the table shows at once that the colors of all of the enamel specimens are perceived by all of the observers as "blue", "green", "blue-green", or "green-blue", which, in general, is what would be expected from the data on selectivity of reflectance as given in figures 6, 7, and 8. On the basis of the data given under the caption "blue/green ratio" in table 4, we may perhaps summarize the results given in this table by the following compromise answers:

Specimen	Hue
63, 79, 114	Distinctly bluish blue-green.
92	Bluish blue-green.
48	Blue-green.
4, 29	Greenish blue-green.

It is of interest to note that there is perfect correspondence between these answers and the data on selectivity of reflectance shown in figure 7. The "mean response time" (average time elapsed from the moment the observer began to look until he announced his decision) is of some interest as indicating in a general way how much more readily the observer arrived at a decision for the enamel specimens than for the magnesium carbonate and magnesium oxide.

It will be noted in table 3 that the computed dominant wave length of specimen 4 was found to be 565.4 mμ. This leads us to expect its hue to be yellow-green rather than green or blue-green, as indicated above. Extensive further work was done with this sample and the following conclusion reached: Even for experienced observers, making the most critical judgments possible, the color difference (in a 6° circular field) between specimen 4 and an ideal perfectly nonselective specimen of the same lightness under the same sunlight illumination is a doubtful, vanishingly small difference, the judgment of which results in changing decisions, sometimes the decision that the difference is nonexistent. It is established that the hue of specimen 4 for noon sunlight illumination lies within the spectral segment of the hue circuit between yellow and blue. From a statistical point of view, we may say that the hue of specimen 4 is most probably green, but that it may be either yellow-green or blue-green, dependent upon the brightness of the specimen field relative to the brightness of the comparison field, and also upon uncontrollable and unknown changes within the observer. Therefore, insofar as they can be made and have any significance, the direct comparisons of colors (as colors) are in accord with the data on selective reflectance; but the indications of the latter are more definite and subject to less uncertainty and ambiguity. As the departure of the specimen from perfect nonselectivity becomes progressively smaller the indications of color computed from measurements of spectral reflectance retain definiteness after the directly observed departure from gray by color sense in a 6° circular field divided along a diameter has become indeterminate.

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THERMAL DECOMPOSITION OF TALC

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ABSTRACT

A nearly pure talc was investigated both unheated and after heating at numerous temperatures ranging up to 1,435° C. The studies included the measurement of heat effects, weight losses, and changes in true specific gravity occurring on heating talc. X-ray and microscopical examinations were made of the heated samples.

There was no change in the crystal structure of the talc up to 800° C. At 800 to 840° C the talc decomposed to enstatite, amorphous silica, and water vapor. The enstatite gradually changed to clinoenstatite around 1,200° C, and the amorphous silica changed to cristobalite around 1,300° C, giving clinoenstatite and cristobalite as final products.

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I. INTRODUCTION

Talc, both pure and combined with fluxing and with bonding agents, has been used for many years by ceramists in the manufacture of specialties. More recently, interest in talc as an ingredient of whiteware and of clay refractories, especially saggers, has resulted in technical studies of its potentialities.

Because of the promising results reported in recent literature and the probability of the increasing use of talc in the ceramic industry, it seemed desirable to have fundamental data on the process and products of its thermal decomposition. This report is the result of an investigation in which such data were obtained.

II. MATERIALS

The talc, from Manchuria, has the following chemical composition: [1] MgO, 32.32 percent; SiO_2, 61.34 percent; CaO, trace; R_2O_3 (mostly Al_2O_3), 0.71 percent; ignition loss, 5.81 percent. Petrographic examination shows at least 95 percent to have the correct indices of refrac-

[1] Analyzed by A. S. Creamer and reported in the J. Am. Ceram. Soc. 18, 259 (1935).

tion for talc, as given by Larsen and Berman.[2] Whether the small amount of R_2O_3 be ignored, or whether it be assumed to be present as Al_2O_3 in kaolinite, the molecular ratio of MgO, SiO_2 and H_2O is very close to 4:5:1.54. This molecular ratio is of interest because it should throw some light on the controversial question of the true formula of talc,[3] since this talc exceeds in purity any heretofore reported in the literature, as far as known to the authors.

Reference materials used in preparing comparison X-ray patterns included the magnesium silicates and several forms of silica. Of these, only the clinoenstatite (monoclinic $MgO{\cdot}SiO_2$), enstatite (orthorhombic $MgO{\cdot}SiO_2$), and cristobalite (the high temperature form of SiO_2) will be described. The clinoenstatite was a pure artificial product.[4] The enstatite was from Espedalen, Norway, and according to chemical analysis [5] contained 6.43 percent of FeO replacing MgO. Despite the impurity, the X-ray pattern is probably identical with that of pure enstatite since there is very little change in lattice dimensions in the enstatite-hypersthene solid-solution series. The cristobalite was an artificial product prepared by heating pure silica gel at 1,400° C.

III. METHODS AND RESULTS

1. HEAT EFFECTS

Thermal effects were observed by the differential thermocouple method with α–Al_2O_3 as the reference material. Readings of emf, generated by a couple composed of Pt and Pt—10-percent Rh wires, were taken at 1-minute intervals by means of a K-type potentiometer. The furnace temperature was varied at the practically constant rate of 6° C per minute.

One set of data is plotted in figure 1, the ordinates being the galvanometer deflections representing the temperature difference between the neutral body and the sample, and the abscissas being the temperatures of the sample. In a total of six such heating curves, the minima of the heat effects were reproduced within ±3° C. The plot [6] shows two endothermic effects, a small one from about 530 to 572° C and a larger one from about 860 to 953° C. The reactions causing both heat effects were irreversible.

2. WEIGHT LOSSES

Weight losses were determined on 1- to 10-g samples heated in platinum containers at the temperatures, and for the intervals of time, given in table 1. The losses, calculated in terms of percentage of the original weight of the sample, are given in table 1 and plotted in figure 1. Each value represents a single determination.

[2] The Microscopic Determination of the Non-Opaque Minerals, U. S. Geological Survey Bul. 848 (1934).
[3] N. H. and A. N. Winchell, Elements of Optical Mineralogy, part II (John Wiley & Sons, Inc., New York, 1927).
[4] Prepared from fusion by N. L. Bowen and J. F. Schairer of the Geophysical Laboratory.
[5] H. S. Washington and H. E. Merwin, Am. Mineral 8, 64 (1923).
[6] The general downward trend of the curve is due to the peculiarities of the apparatus, such as the placement of the thermocouple junctions, the centering of the platinum container in the furnace tube, etc.

TABLE 1.—*Relation of temperature and time of heat treatment to weight loss, true specific gravity and crystal structure of talc*

Temperature of heating	Time of heating	Weight loss	True specific gravity $\frac{25°}{25°}$	Crystalline phases indicated by X-ray pattern
°C	hr	*Percent*		
Unheated			2.78	
340 ± 3	18	0.10	2.78	
380 ± 3	22	.18		
420 ± 3	22	.50		
450 ± 3	22	.84		
480 ± 3	23	.94		
520 ± 10	20	1.07	2.80	
772 ± 3	16	1.34	2.81	Talc.
782 ± 3	20	1.40		
795 ± 2	18	1.74	2.83	Do.
806 ± 2	17	2.45		
816 ± 2	24	3.77		
825 ± 2	18	4.58		
840 ± 2	20	5.42	2.91	Enstatite.
900 ± 2	24	5.49		
1,000 ± 10	17		2.94	Do.
1,200 ± 10	2	5.80	2.96	Enstatite, +clinoenstatite.
1,300 ± 10	4	5.80	2.96	Clinoenstatite, +cristobalite.
1,435 (cone 17)	5	5.86	3.01	Do.

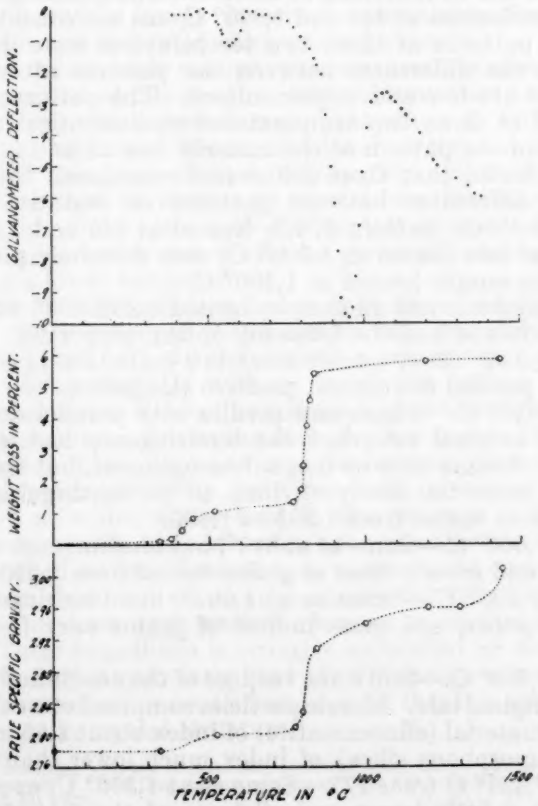

FIGURE 1.—*Typical heating curve, and curves showing weight loss-temperature and true specific gravity-temperature relations for a nearly pure talc*

3. VOLUME CHANGES

The true specific gravity of the unheated and of heated samples was determined in general according to the American Ceramic Society standard method.[7] A 25-ml picnometer and 5-g sample of the talc were used, and the determinations were made at 25 ±0.01° C.

Since talc which has not been strongly ignited is very slowly wet by water, care must be taken to see that all of it is under the water after the boiling treatment. The results are given in table 1 and plotted in figure 1. Each value is the average of two determinations, which agreed within 0.002.

4. X-RAY AND MICROSCOPICAL EXAMINATIONS

Determinations of the crystalline compounds present in the heated samples were made by comparison of X-ray powder diffraction patterns. Copper K-radiation from a demountable ion-type tube and a camera of 4.1-cm radius were used. The camera was divided so that comparison patterns of the test and reference materials could be photographed on the same film. Supplemental examinations of the talc samples were made with the petrographic microscope.

The results are summarized in table 1. The presence of enstatite in the samples heated at 840 and 1,000° C was not considered certain because the patterns at these two temperatures were quite diffuse, and because the differences between the patterns of enstatite and clinoenstatite are few and unpronounced. The patterns of the material heated at these two temperatures were identical and differed definitely from the pattern of the material heated at 1,300° C. The evidence indicated that these differences correspond with the more pronounced differences between patterns of enstatite and clinoenstatite. Both the pattern of talc heated at 840 and 1,000° C, and the pattern of talc heated at 1,300° C, were definitely present in the pattern of the sample heated at 1,200° C.

The unheated talc and all samples heated below 800° were identical microscopically and had the following optical properties:

$\alpha=1.539\pm0.001$; $\beta=\gamma=1.589\pm0.001$; $\gamma-\alpha=0.050$; $(-)2V$=practically zero; parallel extinction; positive elongation.

Heated at 840° C.—Plates and needles with parallel extinction the same as the original talc, but the birefringence had decreased to about 0.010. Grains were no longer homogeneous, but the individual components were too finely divided to be distinguished. Gross indices of grains varied from 1.585 to 1.595.

Heated at 1,000° C.—Same as at 840°, but birefringence was reduced still further, and gross indices of grains varied from 1.590 to 1.600.

Heated at 1,200° C.—Same as at 1,000°, but birefringence was reduced still further, and gross indices of grains vary from 1.595 to 1.610.

Heated at 1,300° C.—Still some vestiges of the needle and plate structures of the original talc. Mosaic particles composed of weakly birefringent matrix material (clinoenstatite) of index about 1.65 and isotropic inclusions (amorphous silica) of index much lower than the matrix.

Heated to 1,435° C (*cone 17*).—Same as at 1,300° C, except that the crystals were a little larger and all trace of the talc structure had disappeared.

[7] J. Am. Ceram. Soc. 11, 453 (1928).

IV. DISCUSSION

The large endothermic heat effect at 860 to 953° C is obviously associated with the weight loss and increase in specific gravity between 800 and 840° C.[8] The X-ray patterns show that, below the temperature range of rapid loss of water, the material retains the same crystal structure as the unheated talc. They also show that the sample heated at 840° C, which has undergone the larger and comparatively rapid loss in weight, has changed to enstatite and (probably) amorphous silica according to the reaction: $4MgO{\cdot}5SiO_2{\cdot}H_2O \rightarrow 4(MgO{\cdot}SiO_2)+SiO_2+H_2O$.

Enstatite appears to remain the only crystalline phase up to about 1,200° C, at which temperature a gradual inversion to clinoenstatite is evidently in progress. This is in agreement with the results of Bowen and Schairer,[9] [10] who place the inversion point between enstatite and clinoenstatite at about 1,145° C, and state that the inversion attains a measurable rate at temperatures only a few degrees above 1,145° C.

Since cristobalite first appeared at 1,300° C, it is evident that the silica present in excess of the 1:1 ratio remained in the amorphous condition up to some point between 1,200 and 1,300° C. This is the general temperature range in which cristobalite first appears in heated kaolin and in heated silica gel and glass.[11]

When heated to high enough temperatures the final products of the decomposition of talc are therefore clinoenstatite and cristobalite.

The relatively small endothermic heat effect at 530 to 572° C is probably associated with the smaller loss in weight at 380 to 450° C. The cause of this heat effect is not readily apparent. The X-ray patterns show that no change in crystal structure has taken place. Therefore, the effect cannot be due to loss of water in the crystal lattice and adsorbed water would be given off more gradually and probably at a lower temperature.

The most plausible explanation is that advanced by Foshag and Wherry.[12] They observed that a certain talc containing 2 molecules of water lost about half of this water when heated "to a dull red heat" (probably about 600° C) without losing its optical homogeneity. The remaining water was lost at a much higher temperature and with loss of homogeneity. Reasoning from the low degree of hardness and platy character of talc, they assumed the water in excess of 1 molecule to be held electrostatically between basal cleavage planes. The temperature at which water held in this manner is lost should be intermediate between that of water bound in the crystal lattice and that of adsorbed water. Loss of such water should cause only a small change in volume and no change in crystal structure, and hence should not produce any marked changes in optical properties or density. Their hypothesis is strongly supported by the data in this paper which show particularly that (1) the change is accompanied by a small, but reproducible heat effect, and (2) that it is not accompanied by any change in crystal structure.

[8] Heat effects associated with loss of chemically combined water usually appear in heating curves at temperatures about 100° C higher than the temperatures at which this water is lost under static conditions.
[9] Am. J. Sci. **29**, 151 (1935).
[10] Krause states that clinoenstatite forms at about 900° C. Ber. deut. keram. Ges. **10**, 94 (1929).
[11] R. B. Sosman, The Properties of Silica, p. 97-9, 473-5 (The Chemical Catalog Co., New York, N. Y., 1927). R. A. Heindl, W. L. Pendergast, and L. E. Mong, B. S. J. Research **8**, 199 (1932) RP410. H. Insley and R. H. Ewell, J. Research NBS **14**, 626 (1935) RP792.
[12] Am. Mineral. **7**, 167 (1922).

According to Gruner's [13] recent work on the crystal structure of talc, the unit cell of talc contains 12 Mg, 16 Si and 48 O atoms, corresponding to a simplest formula $3\ MgO{\cdot}4SiO_2{\cdot}H_2O$. This would indicate that water in excess of one molecule has a random arrangement and does not diffract X-rays. While Gruner's result conflicts with the $MgO{\cdot}SiO_2$ ratio of 4:5 found for the Manchurian talc, it does support the evidence in this paper that one molecule of water is bound in the lattice and behaves differently from water in excess of one molecule. However, support from Gruner's work loses some weight since he does not give an analysis of the talc he used.

V. SUMMARY

A sample of a nearly pure talc was investigated both unheated and after heating at 18 temperatures from 340 to 1,435° C. The studies made included the determination of heat effects, weight losses, and changes in true specific gravity occurring on heating talc. X-ray and microscopical examinations were made of the heated samples.

Water in excess of 1 molecule was mostly driven off between 380 and 500° C. This water loss was accompanied by a small endothermic heat effect, but not by any change in crystal structure or optical properties.

The molecule of combined water was driven off between 800 and 840° C. This water loss was accompanied by a large endothermic heat effect and an increase in true specific gravity from 2.83 to 2.91, and by breakdown of the talc into enstatite and amorphous silica.

Inversion of the enstatite to clinoenstatite took place gradually, both phases being observed in material heated at 1,200° C, and only clinoenstatite in material heated at 1,300° C. The material heated at 1,300° C also showed conversion of the amorphous silica to cristobalite. Thus, the final products of the thermal decomposition of talc are clinoenstatite and cristobalite. There was a further gradual increase in the true specific gravity from 2.91 to 3.01 on heating from 840° up to the highest temperature, 1,435° C.

The data support the hypothesis of Foshag and Wherry that water in talc in excess of 1 molecule is not constitutional and may be held electrostatically between basal cleavage planes.

[13] Z. Krist. 88, 412-9 (1934).

WASHINGTON, September 11, 1935.